SOIL SCIENCE

Founded 1916 by Jacob G. Lipman

Editor-in-Chief
FIRMAN E. BEAR

Associate Editor
HERMINIE BROEDEL KITCHEN

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NOTICE

The index and volume contents for Volume 54 will appear
in the first (January 1943) number of Volume 55.

(*Soil Science*)

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CONSULTING EDITORS

ANALYSES AND PROFILE NOTES OF SOME LATERITE SOILS AND SOILS WITH IRON CONCRETIONS OF THAILAND

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Royal Department of Agriculture, Bangkok, Thailand

Because of the scarcity of data relating to equatorial soils it seems particularly desirable that certain data collected during the last few years in the study of the soils of Thailand be placed on record. It is believed that these data substantiate previous observations (15) as to certain misconceptions concerning laterites and some other soils of equatorial regions.

FIELD AND LABORATORY DATA ON LATERITE AND LATERITIC SOILS

Because Thailand, occupying a central part of the East Asian peninsula of Indo-China, lies between about 6° and 21° north latitude, her soils are all within the tropical zone. Since much of the kingdom, however, has a long and fairly intense annual dry season, the climate of this country as a whole differs greatly from the popular conceptions of "tropical," and for this reason the soils might better be called "equatorial" (13).

During the last 6 years the senior author has traveled widely in Thailand, studying soils, agricultural questions, and other land-use problems in the field. Often it has been necessary to report on the agricultural possibilities of the soils of certain districts and as to whether or not such lands might be more effectively utilized in some new or different agricultural program. In order to make a fair appraisal promptly, it has been necessary to place more than the usual reliance on field-discernible characteristics of the soils under survey. This has been because in only a very few cases have field experiments been carried out upon possible new crops or new agronomic practices. Nor have there been facilities for making greenhouse or pot culture tests for evaluating the plant-producing capacity or the fertilizer response of even important soil types. Furthermore, because of limited laboratory facilities even the chemical and physical analyses of soil samples have often lagged far behind the field work. Field criteria were imperative, therefore, for reliable estimates of the character of the soils of a region and their capacity to produce crops. In this soil appraisal in Thailand the presence of laterite, in the restricted original sense, has proved very useful because it is a soil horizon characteristic of the senile or final stage of soil development and one very easily distinguished in the field (8, 12, 13). The presence of a laterite horizon in the profile is a danger signal, indicating that the weathering processes have already run to completion and that plant nutrients originally present in the soil materials either have been almost completely carried away by the leaching processes or have been locked up in insoluble precipitates.

[1] Soil scientist, Department of Agriculture, Ministry of Agriculture; and chief, Division of Agriculture Science, Department of Science, Ministry of Economics, respectively.

Over a large part of Thailand the parent rocks or other parent materials from which the soils have been formed are weathered to a depth of many meters. It is impossible, therefore, not only to learn the nature of the parent materials but usually to get more than a glimpse of the uppermost parts of the soil profile. Weathering has proceeded far, and even geologic or normal erosion has been too slow to rejuvenate the soil by removing the impoverished uppermost parts of the profile. Particularly under such circumstances, the presence of a laterite horizon in the soil profile has proved a most useful criterion of soil character.

Descriptions of a number of profiles of Thailand soils are given in table 1, and their analyses, in table 2. Some of these profiles are of laterite soils, that is, soils which contain a true laterite horizon; some are of tropical loams; and with one exception the remainder are of soils that in some countries would be called "shot" or "ironstone gravel" soils (1, 16, 19), that is, soils of which one or more horizons contain a considerable proportion of iron concretions. These last-mentioned profiles are included in this paper on laterite soils because it is apparent that in at least some of them the concretionary horizon represents an early stage in the development of a pisolitic type of laterite horizon. Samples of similar soils are from other localities where probably not enough iron has been available in the parent materials for development of a true laterite horizon. Whether or not further studies of the laterite soil problem will support all these assumptions, similarities in the proportions of Si, Fe, and Al in laterites of Thailand (15) and in the discrete concretions of soil profiles reported upon in this paper are interesting.

Particular attention is directed to the colors of the eluvial (i.e., lixivium) horizons as given in table 1. Below the surface darkening of 10 to 20 cm. by organic matter, the colors of the profiles in sandy regions are very light, in fact, a very light brown, a cream, or a dirty white in many cases. The eluvial horizons overlying the laterite horizons are usually thoroughly leached (lixiviated); if these horizons contain a large proportion of quartz sand,[2] their color will usually be well bleached if not nearly white. Just because it is bleached, such a white lixivium horizon should *not* be called "podzolized." Nevertheless, many temperate-zone pedologists would at once so designate it, in spite of the fact that the profiles described in this paper are those of laterite soils or lateritic soils which have, or are developing, laterite horizons. In these profiles there is no indication of any illuvial podzol horizon development at all. As discussed later in more detail, the use of "podzolized" should be restricted to lixiviation processes that are known to be producing a true podzol profile, which to be typical must include the *organic*-iron illuvial horizon—a type of accumulation never known to develop in a laterite soil profile. In connection with the profiles considered in this paper, it is not admitted that there could have been any change in the climate. Hence, there is *no* reason for believing that in these cases the laterite profile developed under a previous and different climate, or that under the present climate podzolization, not laterization, is the process that is taking place.

COLLECTION AND NUMBERING OF SAMPLES AND THEIR ANALYSIS

In sampling Thailand soils an endeavor is always made to collect a sample of each horizon. Any apparent change in color, texture, or structure is considered sufficient reason for collecting a separate sample to show this variation. It should be noted that in tables 1 and 2 all the samples of one profile (from one pit or other single sampling site) carry the same serial number. Following the serial number will be noted "-1," "-2," "-3," etc. These indicate successive samples, each representing a horizon or part of one, and indicating the relative position of the sample in the profile from the ground surface downward (17). The depths between which each sample has been taken are usually given in centimeters, though for deep profiles the depths are sometimes given in meters. Such a method of designating the various parts of a soil profile seems particularly desirable in the early years of the study of soils in a new region, for without laboratory studies it is frequently difficult to decide whether a particular horizon is eluvial or illuvial, and if so, with respect to what substances. Furthermore, in different countries opinion appears to differ as to the significance of the more conventional symbols "A," "B," "C," etc., as applied to various soil horizons—another excellent reason for avoiding their use in this work.

The designation "-L" following the serial number indicates a sample of laterite, commonly one from some ancient ruin; in some instances "-K," "-M," or "-W" has been used. In some earlier collections "-X" was used for laterites. Since the ancient laterite quarries have not been located, naturally the original position of such samples in the soil profile, as well as the depth below the ground surface at which they developed, is not known. The designation "-R" following the serial number has been used for samples of rock. If the serial number of the rock sample is the same as that of a soil sample, the rock sample is believed to represent the parent material of that particular soil profile. [It may be added that serious misconceptions as to the nature of weathering processes, particularly those of laterite soils, have arisen through assuming that the entire profile has developed from a homogenous material represented by the rock or other "parent material" found at the base of the profile (7).]

For the most part, the methods employed by the Agricultural Science laboratory of the Department of Science are those common in British practice.[3]

In considering the analyses of the samples of laterite soils and other profiles reported here, the following points should be kept in mind: 1. The firm laterite mass, as analyzed and reported in the tables, represents both the matrix material and the precipitated sesquioxides. Though it would have been desirable to separate these two distinct portions manually before chemical analysis, in our work it has been impracticable to do so. 2. It would likewise be desirable to dissect out and analyze separately the red, cellular mass and the whitish clayey

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[3] All the laboratory work was carried out under the supervision of the junior author. Since we have recently received a Beckman glass electrode and hope to be able to present subsequently pH determinations on these and other soils of Thailand, the previous determinations made by means of indicators and/or the quinhydrone electrode are not included in this paper.

TABLE 1

Profiles of laterite, lateritic, concretionary, and related Thailand soils

SERIAL NUMBER	DEPTH	COLORS DRY (D) AND MOIST (M) AND TEXTURE*	LAND USE, AND PLACE OF COLLECTION
	cm.		
88-1	0–10	Light pinkish gray (D), light pinkish brown (M), light sandy loam.	Open, dwarf dipterocarpus forest. Lan Hoi Township, Sukotai Province [cf. (13, fig. 10)].
88-2	10–15	Light pinkish gray (D), light pinkish brown (M), gravelly loamy sand (gravels are iron concretions). This horizon of variable depth, overlying the laterite.	
88-3	15–25	Cemented masses of laterite, like the "heads" which appear above the surface occasionally.	
96-1	0–15	Brownish gray (D), dark gray (M), fine sandy loam.	*Dōng* forest near canal. Maecho, Sansai Township, Chiengmai Province, Northern Thailand.
96-2	15–50	Brownish gray (D), pinkish gray (M), light fine sandy loam.	
96-3	50–100	Very light pinkish brown (D), light pinkish brown (M), light fine sand.	
98-1	0–11	Light pinkish brown (D), pinkish brown (M), very fine sandy loam.	Poorly drained tobacco field. Maecho, Sansai Township, Chiengmai Province, Northern Thailand.
98-2	11–33	Light pinkish brown (D&M) very fine sandy loam.	
98-3	33–59	Light pinkish brown (D&M) very fine sandy loam with a few medium hard concretions.	
98-4	59–100	Very light pinkish brown finely mottled and speckled with brown (D), light pinkish brown (M), loam with some iron concretions and a few masses of laterite.	
101-1	0–14	Light grayish brown (D), grayish brown (M), light silty clay loam.	Padi field. Maecho, Sansai Township, Chiengmai Province, Northern Thailand.
101-2	14–42	Light pinkish gray with some brown spots (D), light pinkish grayish brown (M), light clay loam.	
101-3	42–80	Light pinkish gray with some brown spots (D), light pinkish grayish brown (M), clay loam.	
101-4	80–95	Laterite chunks and masses: brown, light brown, dark, etc. inside, in a matrix of clay loam like the overlying horizon.	
102-1	0–20	Finely mottled light brown on pinkish gray (D), medium brownish gray (M), light clay loam.	Padi field sample. Maecho, Sansai Township, Chiengmai

*Textures judged by the usual "thumb and finger" test.

TABLE 1—*Continued*

SERIAL NUMBER	DEPTH	COLORS DRY (D) AND MOIST (M) AND TEXTURE*	LAND USE, AND PLACE OF COLLECTION
	cm.		
102-2	20–60	Dirty white (D), light brownish gray (M), heavy loam.	Province, Northern Thailand.
102-3	60–75	Dirty white gravelly clay loam, the gravels being concretions; black and brown inside (D), light brownish gray (M). Also chunks of laterite.	
104-1	0–22	Brownish gray (D), dark brownish gray (M), light fine sandy loam.	Teak forest. Maecho, Sansai Township,
104–2	22–58	Light pinkish or dirty white (D), grayish brown (M), fine sandy loam with a few hard iron concretions.	Chiengmai Province, Northern Thailand.
104-3	58–111	Light pinkish or dirty white (D), light grayish brown (M), gravelly loam; all the more numerous and larger gravels are iron concretions.	
149-1	0–15	Grayish finely mottled with light brown (D), dark grayish brown (M), fine sandy loam.	Padi field. Nam Awm Township, Sisaket Province,
149-2	20–45	Gray (D&M) gravelly clay loam, the gravels being iron concretions.	NE Thailand.
	45–100	Boring shows more and more concretions, to almost a solid mass at 1m.	
150-1	0–10	Pinkish gray (D), brownish gray (M) fine sandy loam.	Open forest on a low hill. A few kilometers north
150-2	35–45	Light brown (D), light grayish brown (M) loam.	of sample site 149. Nam Awm Township Sisaket
	45–100	Boring shows that the texture gradually grades into a clay loam at 100 cm. Masses of uncemented limonite concretions exposed in shallow erosion of the nearby cart track.	Province, NE Thailand.
151-1	0–12	Dark reddish brown (D), chocolate-brown (M), light clay loam.	Well-forested low hill. A few kilometers north
151-2	65–90	Bright brownish red (D), reddish brown (M), light clay loam.	of sample site 150. Nam Awm Township,
151-R	100	Parent rock (andesitic?) a magmatic extrusion.	Sisaket Province, NE Thailand.
155-1	0–20	Light pinkish gray with light brown spots (D), brown (M), light very fine sandy loam.	A recently excavated pit (cf. fig. 7). Ban Kam Paeng
155-2	100–130	Finely mottled: light pinkish gray, light brown, brown etc. (D), yellowish brown (M), gravelly clay loam.	railroad station. Sisaket Province, NE Thailand.

TABLE 1—*Continued*

SERIAL NUMBER	DEPTH	COLORS DRY (D) AND MOIST (M) AND TEXTURE*	LAND USE, AND PLACE OF COLLECTION
	cm.		
155-3	200–240	Various shades of browns (D), brown, light brown, dark brown, light bluish, etc. (M), concretionary gravels.	
155-4	250–280	Light bluish white (D), light yellowish white (M), light clay loam.	
155-5	300–330	Purplish (D), dark purplish (M), soft sandstone (fine sandy loam). It is presumably from this very widespread Tertiary sandstone that the pink sand and fine sand have come which are so characteristic of so many of Thailand's sandy laterite soils.	
160-X	about 10 m.	Laterite chunks: brown black, etc. The matrix soil light yellowish brown (D), light brownish yellow (M), sandy loam.	From a recently dug well. About 4 km. NW of Ubon town, Ubon Province, NE Thailand.
168-X	100	Reddish brown (D&M) gravelly clay, loam, the gravels being iron concretions, in places cemented into larger masses.	Gravels quarried for road surfacing after screening. About 4 km. north of Mahasarakam town, NE Thailand.
177-1	0–10	Gray (D&M) light fine sandy.	Open, dwarf forest near the top of a long gentle slope. 24 km. north of Khon Kaen, NE Thailand (see fig. 1).
177-2	50–70	Light pinkish brown (D&M) light fine sand.	
177-3	50–75	Hard laterite intermediate type, between vesicular and coarsely pisolitic, being quarried locally for road metal. Masse are found at irregular depths, from the surface to a meter or more below.	
308– 310, 312,	0— 5–20 6–20— 30–50	Light brownish gray (D), brownish gray (M), silt loam to loam. Grayish brown, browns, or yellows (D), grayish brown, yellowish brown or red (M) gravelly clay loam.	These six profiles were collected within an area 200 by 600 m. North and northeast of Padang Besar railway station close to the boundary of Malaya, Songkla Province, Southern Thailand.
313	40–60— 60–100	Light red with some light bluish (D), light red to red (M), gravelly clay loam.	
310-4	75–100	Represents a deeper horizon than reached in other profiles of the locality (probably the influence of the parent material). Purplish with light bluish (D), slight purplish red (M), clay loam.	
354-1	0–20	Red (D&M) clay; a "tropical loam."	Hevea rubber plantation. 2 km. north of Trang
354-2	25–42	Red (D), bright red (M), clay.	

*Textures judged by the usual "thumb and finger" test.

TABLE 1—*Continued*

SERIAL NUMBER	DEPTH	COLORS DRY (D) AND MOIST (M) AND TEXTURE*	LAND USE, AND PLACE OF COLLECTION
	cm.		
354-3	75–100	Red (D), bright red (M), gravelly clay loam.	town, Southern Thailand.
355-1	0–15	Light grayish brown (D), grayish brown (M), fine sandy loam.	Very poor Hevea rubber trees. 16 km. north of
355-2	15–30	Light yellowish brown, slightly variegated (D), yellowish brown (M), heavy fine sandy loam.	Trang town, Southern Thailand.
355-3	33–45	Light brown, brown, with some dark brown, and red (D), yellowish brown (M), concretionary gravels.	
358-1	0–20	Light brownish gray (D), grayish brown (M), loam.	Good rubber trees: this soil contains some P_2-
358-K	25–100	Light yellowish brown (D), yellowish brown (M), gravelly clay loam. The gravels are concretions, dark colored inside.	O_5; sample 355, practically none. 17 km. north of Tungka, Phuket Island, Southern Thailand.
361-1	0–6	Grayish brown (D&M) loam.	Bamboo forest.
361-2	18–68	Light brown (D), yellowish brown (M), clay loam.	Taichang Township, Pangnga Province,
361-3	90–135	Reddish brown (D), brownish red slightly mottled (M), clay loam.	Southern Thailand.
361-4	165–175	Red and light yellowish brown (D), brownish red (M), gravelly clay loam (of small concretions).	
372-1	0–10	Brownish gray (D), dark brownish gray (M), sandy loam.	Abandoned clearing grown up with brush
372-2	20–30	Brown (D&M) loam.	and *Eupatorium odora-*
372-R	50–70	Red (D&M) rather soft, weak laterite with a purplish red interior, possibly the remains of the parent material color.	*tum.* ½ km. south of Tapli, Kraburi Township, Ranong Province, Southern Thailand.
401-1	0–20	Light brownish gray (D&M) fine sandy loam.	Bamboo and former clearings. Glaeng Township, Rayong Province,
401-2	100–125	Light brown (D&M) light clay loam.	SE Thailand.
401-3	150–175	Reticulated bluish and brownish (D), red and light brown (M), clay loam with round iron concretions, "rather soft laterite."	
401-4	175–200	Bluish, light brownish and brownish (D), angular fragments purplish inside (M), "hard laterite exposed in the bottom of the trail."	

TABLE 1—*Continued*

SERIAL NUMBER	DEPTH	COLORS DRY (D) AND MOIST (M) AND TEXTURE*	LAND USE, AND PLACE OF COLLECTION
	cm.		
408-1	0–10	Brownish gray (D), dark grayish brown (M), light fine sandy loam.	Forest. NW Tamai Township, Chantaburi Province, SE Thailand.
408-2	25–40	Light brown (D), brown (M), light fine sandy loam.	
408-L	2 m.	Laterite, exposed in creek bank about 50 m. from sample pit.	
418-1	0–10	Dark grayish brown (D), dark brownish gray (M), loam, with angular concretions and laterite fragments.	Tall tropical forest, on land but a few meters above sea level. Kradat Island, Trat Province, SE Thailand.
418-2	12–36	Laterite chunks making a stony loam with a little grayish brown earth.	
418-3	40–60	Laterite chunks with a little grayish yellow (M) clay loam.	
420-1	0–20	Light reddish brown (D), reddish brown (M), finely granular clay loam.	In coconut and pineapple plantation. Mak Island, Trat Province, SE Thailand.
420-2	40–60	Light reddish brown (D), reddish brown (M), gravelly clay loam.	
420-3	85–105	Brown (D&M) gravelly clay loam (gravels are concretions).	
420-4	110	Red and brown hard concretions and possibly some partly weathered parent rock, which appears to be basaltic. The concretions are masses of more or less spherical concretions, *not* vesicular (because developed above water-table?).	
440-1	0–12	Light gray with brown threads (D), brownish gray (M), silt loam.	Abandoned padi land. Central Township, Trat Province, SE Thailand.
440-2	15–25	Bluish with light brown threads and fine mottling (D), light brownish gray (M), light silty clay loam.	
440-3	50–75	Light brown, brown, etc. (D), light brown (M), gravelly clay loam.	
444-1	0–15	Light brownish gray (D), dark grayish brown (M), loam.	Profile exposed at river bank. Khao Saming Township, Trat Province, SE Thailand. Because of flooding annually, likely the surface soil is younger than the deeper portions of the profile.
444-2	40–60	Light grayish brown (D), brown (M), light clay loam.	
444-3	100–125	Light grayish brown with red inside (D), light reddish brown (M), clay loam.	
444-4	300–325	Reds, light blues, etc. (D&M) laterite more of the vesicular type.	
444-5	325–350	Red and light blue (D), variegated (slightly purplish when moist) clay loam.	

*Textures judged by the usual "thumb and finger" test.

TABLE 1—*Continued*

SERIAL NUMBER	DEPTH	COLORS DRY (D) AND MOIST (M) AND TEXTURE*	LAND USE, AND PLACE OF COLLECTION
	cm.		
486-1	0–20	Light grayish brown (D), grayish brown (M), fine sandy loam.	From slight elevation in new pepper garden. Makam Township, Chantaburi Province, SE Thailand.
486-2	15–30	Light brown (D), brown (M), loam.	
486-3	45–55	Light brown (D), brown (M), gravelly loam.	
544-1	0–10	Brownish gray (D), dark brownish gray (M), granular clay loam.	Forest of teak, *tabac*, bamboo at footslope of limestone bluff. Elevation 927 m. 52 km. northeast of Lampang, Northern Thailand.
544-2	20–40	Chocolate-brown (D&M) clay loam.	
544-M	60–80	Deep reddish brown (D), chocolate-brown (M), gravelly loam.	
551-1	0–20	Light pinkish grayish brown (D), grayish brown (M), sandy loam.	Recently cleared scrub forest. Government sugar cane plantation. Gaw Ka Township, Lampang Province, Northern Thailand.
551-2	40–60	Light pinkish brown (D&M) sandy loam.	
551-3	95–115	Pinkish, brownish, etc., slightly consolidated lateritic concretions, of an intermediate type between pisolitic and vesicular.	
576-1	0–25	Brown (D), reddish brown (M), gravelly loam, with smooth concretions.	Pineapples and bamboo on low hill about 3 m. above level of padi plain. Central Township, Chantaburi Province, SE Thailand.
576-2	40–50	Upper portion of the solid laterite, very hard: reddish brown, brown, dark, etc. (D&M) vesicular type.	
576-3	115–125	Lower portion of the laterite being quarried in this pit. Local residents report that laterite in this quarry could be worked considerably deeper.	
620-1	0–15	Light brown (D&M) loam.	Culled forest 6 km. east of south of saw mill at Gaw Karoan. Panom Sarakam Township, Chachoengsao Province, Central Thailand.
620-2	15–30	Reddish brown (D&M) gravelly loam.	
620-3	50–65	Reddish brown (D) brownish red (M) gravelly loam; concretions semi-angular.	
626-1	0–10	Brownish gray (D&M) loam.	Top of low hill, from the base of which sample 625-L was collected. Dong Praram. Prachinburi Province, Central Thailand.
626-2	10–30	Light brown (D), brown (M), clay loam.	
626-3	35–55	Brown and black (D), dark brown and black (M), subangular gravelly loam.	
633-1	0–18	Grayish brown (D), dark grayish brown (M), loam.	Fruit gardens south of Tatum Market. Srima-

*Textures judged by the usual "thumb and finger" test.

TABLE 1—*Concluded*

SERIAL NUMBER	DEPTH	COLORS DRY (D) AND MOIST (M) AND TEXTURE*	LAND USE, AND PLACE OF COLLECTION
	cm.		
633-2	18–40	Brown (D), brown and black (M), gravelly loam. Farmers here say the solid laterite is about 2 m. below the surface.	hapot Township, Prachinburi Province, East Central Thailand.
670-1	0–10	Light brownish gray (D), brown (M), light fine sandy loam.	Grassland with scattering clumps of brush on
670-2	10–50	Light brown with black concretions (D&M) gravelly loam.	slight elevation. Central Township,
670-X	75 ?	Chunks of laterite from heap for road metal, excavated from this soil.	Nongkhai Province, NE Thailand.
695-W	5½ m.	Light bluish, pinkish, yellow, etc. clay and hard laterite masses. Tubules with light bluish clay seem to be developing through the lateritic concretions.	Large iron concretions from well. 1 km. northwest of Ubon town, Northeastern Thailand.
767-1	0–15	Brownish gray (D), grayish brown (M), loam (with concretions).	Heavily culled forest on low elevation. 9 km.
767-2	15–40	Hard laterite as exposed in nearby highway cut.	north of Prae, Northern Thailand [Cf. (13,
767-3	80–110	Laterite.	figs. 9 and 18).]
771-1	0–30	Brown (D), grayish brown (M), sandy loam.	2 km. NE of Denjai railway station. Prae
771-2	80–110	Laterite, very firm, requiring much effort with heavy pick to break out the sample.	Province, Northern Thailand.

*Textures judged by the usual "thumb and finger" test.

materials in the interstices of lateritic materials. 3. In equatorial soils the percentages or ratios of Fe, Al, and Si compounds in the colloidal clay are *not*, necessarily, an index of the degree of weathering, for in laterite soil profiles a very large proportion of the sesquioxides has been precipitated and exists as noncolloidal concretionary or accretionary masses of laterite or as discrete concretions. 4. Since these analyses have been made by fusing the entire sample, the proportions of quartz and other silicon compounds have not been determined. We feel (15), however, that many writers have placed far too much emphasis upon "resilication" and other *supposed* movements of Si compounds in the laterite soil profile. With Milne (7), we believe that in most cases the differences in the amounts of Si found by analysis in various parts of the profile are the result of differences in the amounts of quartz in different parts of a heterogeneous parent material. It is not likely that variations in amounts of silica in the profile will prove in many instances that there has been any considerable

TABLE 2

Silica, iron, and aluminum in laterite and other soils

Analyses in percentages

SAMPLE NUMBER	"FINE EARTH"				CONCRETIONS AND/OR LATERITE				
	SiO_2	Fe_2O_3	Al_2O_3	SiO_2/R_2O_3 molar ratio	Per cent of sample	SiO_2	Fe_2O_3	Al_2O_3	SiO_2/R_2O_3 molar ratio
A—*Parent materials probably sandstone*									
Khon Kaen									
Province									
177-1	97.8	0.5	1.0	125.					
177-2	98.9	0.3	0.5	245.					
177-3	...	...	...	...	100.0	57.4	28.7	8.9	3.6
Chantaburi									
Province									
Ban Makam									
486-1	85.—	2.2	11.3	11.3	1.1	...	...	...	...
486-2	78.1	3.0	17.0	7.7	4.0	...	...	...	...
486-3	79.1	4.6	11.4	10.1	44.6	28.4	51.5	11.1	1.1
Sukotai									
Province,									
Lan Hoi									
88-1	92.4	2.4	2.9	35.2	7.7	41.3	44.9	7.5	1.9
88-2	92.5	2.1	3.3	33.9	19.7	38.5	46.8	8.3	1.5
88-3	76.5	14.1	7.0	8.0	83.6	38.5	43.9	19.4	1.4
Lampang									
Province,									
Gaw Ka									
551-1	95.9	...	2.0	81.0	2.88	86.9	7.6	2.6	19.8
551-2	95.1	0.98	2.3	55.0	4.45	83.6	9.6	3.1	15.4
551-3	92.3	2.3	2.1	44.0	71.5	58.5	24.9	8.9	4.0
Nongkhai									
670-1	95.4	1.5	1.5	66.0	?	16.4	60.4	12.4	0.55
670-2	83.4	8.3	5.3	13.4		16.1	60.5	14.7	0.51
670-X	...	...	...	...	100.0	26.1	49.8	12.9	0.99
Chantaburi									
Province, NE									
of Tamai									
408-1	92.0	0.6	2.3	58.0	...	...	...	...	...
408-2	93.4	0.8	2.9	46.4	...	...	...	...	...
408-L	...	...	...	...	100.0	35.5	47.0	9.2	1.54
Trat									
Province									
440-1	85.6	0.5	0.7	142.0	2.2	...	...	...	...
440-2	81.1	5.3	9.2	11.0	4.7	...	...	...	...
440-3	60.3	15.7	15.9	4.0	65.1	22.7	53.8	11.4	0.85
Chiengmai									
Province,									
Maecho									
98-1	94.4	0.5	3.0	48.2	...				
98-2	93.2	0.9	4.3	32.4	...				
98-3	94.4	1.5	3.1	39.7	...				
98-4	91.3	0.7	4.0	35.0	29.0	93.8	3.0	1.8	42.7
96-1	93.—	0.17	3.5	43.5	...				
96-2	96.6	0.4	2.3	64.5	1.3	88.4	6.5	2.6	21.9
96-3	98.1	0.2	1.8	86.7	16.7	87.7	7.3	3.3	18.6
102-1	88.7	0.88	7.1	19.6	...				
102-2	88.7	3.0	5.7	19.8	?	52.8	11.7	12.8	...
102-3	78.7	9.1	4.8	12.6	50.2	54.5	19.1	14.2	...
104-1	93.0	3.2	0.56	60.8	...	...	...	...	...
104-2	91.2	1.9	3.3	34.3	4.3	79.0	11.7	6.0	10.0
104-3	89.6	4.4	3.2	25.3	8.8	74.1	16.7	8.7	6.5

TABLE 2—*Continued*

	SAMPLE NUMBER	"FINE EARTH"				CONCRETIONS AND/OR LATERITE				
		SiO_2	Fe_2O_3	Al_2O_3	SiO_2/R_2O_3 molar ratio	Per cent of sample	SiO_2	Fe_2O_3	Al_2O_3	SiO_2/R_2O_3 molar ratio
A—*Parent materials probably sandstone*—Continued										
Chiengmai	101-1	84.8	3.5	5.2	19.3	...	...	...	...	...
Province,	101-2	88.1	3.1	6.1	18.5	...	...	...	...	...
Maecho	101-3	85.4	3.1	7.5	15.2	3.8	57.1	24.3	10.1	3.8
	101-4	76.0	23.2	1.4	8.0	82.6	47.4	33.0	10.5	2.6
Mahasarakam Province, road metal	168-X	72.6	6.7	2.6	18.0	76.3	55.4	26.6	8.7	3.6
B—*Parent materials probably basaltic*										
Sisaket	151-1	42.7	17.3	22.8	2.14					
Province,	151-2	40.7	15.3	32.7	1.62					
Nam Awm	151-R	52.1	10.7	16.8	3.85					
Trat Province,	418-1	31.7	15.8	26.7	1.5	49.8	19.3	39.3	24.0	0.67
Kradat Island	418-2	36.8	18.5	29.5	1.5	55.9	19.2	38.1	26.5	0.64
	418-3	37.0	18.2	30.7	1.5	73.0	19.9	36.9	28.8	0.65
	418-L	...	...	...	...	...	6.2	62.5	15.9	0.19
Trat Province,	420-1	51.0	12.0	23.4	2.8	6.23	nd	nd	nd	...
Mak Island	420-2	51.5	12.6	24.9	2.6	12.8	13.8	39.6	29.5	0.43
	420-3	52.8	9.4	26.2	2.7	31.1	16.1	33.0	33.1	0.53
	420-4	...	...	...	...	100.0	17.0	50.0	20.6	0.55
C—*Parent materials probably limestone*										
Lampang	544-1	43.5	10.2	28.5	2.1					
Province	544-2	42.3	12.5	29.9	1.9					
	544-M	36.3	12.1	34.8	1.5	62.2	14.7	46.5	23.5	0.47
Trang	354-1	40.2	2.2	44.0	1.5	nd	25.7	34.5	28.2	0.87
Province	354-2	40.4	2.2	44.1	1.5	...	...	...	...	...
	354-3	39.0	9.8	38.8	1.47	79.2	20.1	46.9	22.7	0.65
D—*Parent materials probably mixed*										
Trang Province,	355-1	94.0	1.1	1.6	69.4					
Huey Yawt	355-2	91.8	2.2	2.5	59.0					
Township	355-3	86.7	5.0	8.6	12.5	75.0	19.3	60.8	13.1	0.63
Phuket	358-1	53.8	5.3	27.7	3.0	8.7	17.6	54.5	18.4	0.56
Province, 17 km. north of Tungka	358-K	43.6	6.3	37.4	1.8	90.1	13.8	58.5	17.8	0.44

TABLE 2—*Continued*

	SAMPLE NUMBER	"FINE EARTH"				CONCRETIONS AND/OR LATERITE				
		SiO$_2$	Fe$_2$O$_3$	Al$_2$O$_3$	SiO$_2$/R$_2$O$_3$ molar ratio	Per cent of sample	SiO$_2$	Fe$_2$O$_3$	Al$_2$O$_3$	SiO$_2$/R$_2$O$_3$ molar ratio
D—Parents materials probably mixed										
Songkla	308-1	91.8	0.54	3.9	36.8	2.4	28.5	55.1	8.2	1.1
Province,	308-2	84.7	1.7	9.3	13.7	81.4	29.3	54.5	8.2	1.2
Padang Besar	308-3	57.7	3.2	32.4	2.8	32.4	28.4	54.0	9.5	1.1
	309-1	87.7	1.0	5.9	22.6	1.0	20.7	61.7	9.3	0.72
	309-2	62.6	3.6	28.4	3.5	82.5	22.9	57.3	11.3	0.81
	309-3	54.2	3.8	32.9	2.6	40.5	23.2	58.3	9.9	0.84
	310-1	87.4	0.8	6.7	20.6	13.5	nd	nd	nd	nd
	310-2	78.6	2.7	13.7	8.7	77.7	21.6	59.2	10.8	0.77
	310-3	55.4	4.2	27.0	3.1	77.6	23.4	57.2	11.0	0.84
	310-4	55.2	3.3	33.2	2.6	10.8	30.7	46.8	14.7	1.2
	312-1	84.7	1.0	6.2	21.0	13.3	17.1	64.7	11.2	0.55
	312-2	76.1	1.7	12.8	9.3	78.0	19.1	61.7	12.6	0.62
	312-3	54.3	4.2	32.3	2.6	40.4	25.3	52.7	12.7	0.93
	313-1	86.5	1.4	9.7	14.0					
	313-2	80.0	2.0	12.9	9.6	82.1	24.5	57.7	9.3	0.90
	313-3	59.6	2.8	27.7	3.4	23.0	21.8	58.9	9.5	0.79
Sisaket	155-1	90.0	1.1	9.5	15.0					
Province,	155-2	83.4	3.0	8.6	13.2					
Utumpon,	155-3	67.2	10.8	15.4	5.1	74.2	33.5	45.2	12.3	1.4
Bantam Yae	155-4	77.1	1.8	16.2	7.5					
	155-5	56.6	7.7	25.8	3.1					
Sisaket	156-X	42.5	30.4	16.4	2.0	?	21.7	48.7	17.7	0.76*
Province,	157-X	...	...	...	...	100.0	37.3	35.2	12.4	1.8 †
Ban Kamp-										
aeng, laterite										
ruins										
Ubon	160-X	...	...	...	...	100.0	42.1	40.6	8.5	2.1
Province	695-W	...	...	...	...	100.0	48.0	35.0	10.8	2.5
Trat Province,	444-1	80.3	2.8	7.7	14.4					
Khao Saming	444-2	75.—	4.0	16.5	6.7					
	444-3	61.9	6.8	25.3	3.5	24.7	38.0	40.2	12.2	1.7
	444-4	58.8	10.4	24.5	3.2	46.2	34.9	40.7	13.7	1.5
	444-5	60.1	9.2	23.5	3.5					

* Pisolitic.
† Vesicular.

TABLE 2—*Continued*

	SAMPLE NUMBER	"FINE EARTH"				CONCRETIONS AND/OR LATERITE				
		SiO_2	Fe_2O_3	Al_2O_3	SiO_2/R_2O_3 molar ratio	Per cent of sample	SiO_2	Fe_2O_3	Al_2O_3	SiO_2/R_2O_3 molar ratio
D—Parents materials probably mixed										
Chantaburi	576-1	65.6	13.4	11.6	5.5	40.3	35.4	41.0	14.3	1.5
Province, Gaw:	576-2	47.9	20.3	22.6	2.3	84.4	19.4	45.3	20.3	0.67
Kwang, late-	576-3	47.1	21.1	22.6	2.2	79.1	23.4	43.4	20.6	0.82
rite quarry	576-4	...	...	...	...	...	23.7	42.8	20.5	0.84
Prachinburi	626-1	66.5	4.1	16.5	5.9	...	...	...	...	...
Province,	626-2	61.6	4.2	22.0	4.2	8.5	31.4	43.0	17.6	1.2
Dong Praram	626-3	56.1	5.1	27.2	3.1	17.2	20.7	48.3	20.5	0.68
Rayong	401-1	86.8	1.0	8.9	15.4					
Province,	401-2	78.9	1.9	16.2	7.7	1.98	...	...	...	...
Glaeng	401-3	63.1	5.5	26.2	3.6	47.47	27.0	47.1	16.6	0.98
	401-4	66.2	6.6	22.9	4.1	85.36	37.3	36.3	17.6	1.6
Chiengmai	738-L‡	61.7	7.0	22.5	3.9					
Province, Me										
Ing River										
bank, Terng										
Pangnga	361-1	84.7	2.5	8.0	15.0					
Province,	361-2	69.8	5.5	17.6	5.6					
Taichang	361-3	66.1	7.3	18.9	4.8	2.0	29.2	45.4	14.8	1.13
	361-4	95.8	0.3	2.0	74.3	21.9	29.2	44.5	15.1	1.14
Chachoengsao	620-1	81.2	4.6	10.3	10.4	0.7	32.8	45.1	15.1	1.27
Province,	620-2	78.5	6.1	12.3	8.3	39.5	35.2	42.6	14.0	1.44
Panom	620-3	59.8	15.4	20.0	3.4	60.1	31.5	44.2	15.2	1.23
Sarakam										
Prachinburi	633-1	65.8	8.2	16.1	5.2	14.9	18.8	49.6	19.2	0.63
Province,	633-2	58.5	8.8	24.2	3.3	33.1	20.0	46.8	19.2	0.69
Tatum,										
Srimahapot										
	634-L§	...	...	...	...	100.0	33.0	41.5	15.5	1.34
	634-M§	65.9	4.9	22.5	4.3	16.8	74.5	12.0	7.5	8.37
Ranong	372-1	84.9	2.1	6.1	19.3	...	...	...	...	...
Province,	372-2	76.3	4.0	12.9	8.4	...	...	...	...	...
Kraburi Town-	372-R	53.2	16.6	21.1	2.8	42.9	24.9	46.3	16.0	0.93
ship, Tabli										

‡ Depth, 4 m.
§ River bank.

TABLE 2—*Concluded*

SAMPLE NUMBER	"FINE EARTH"				CONCRETIONS AND/OR LATERITE				
	SiO₂	Fe₂O₃	Al₂O₃	SiO₂/R₂O₃ molar ratio	Per cent of sample	SiO₂	Fe₂O₃	Al₂O₃	SiO₂/R₂O₃ molar ratio

SiO_2, Fe_2O_3, Al_2O_3, SiO_2/R_2O_3 molar ratio

Sample	SiO_2	Fe_2O_3	Al_2O_3	SiO_2/R_2O_3 molar ratio	Per cent of sample	SiO_2	Fe_2O_3	Al_2O_3	SiO_2/R_2O_3 molar ratio
D—Parent materials probably mixed									
Prae Province, 9 km. northeast of Prae — 767-1	92.1	2.2	2.4	41.—	32.8	40.6	38.1	10.9	1.96
767-2	...	...	...	...	100.0	46.3	31.3	13.1	2.38
767-3	58.8	20.2	14.4	3.64	80.9	39.3	37.6	13.3	1.8
Prae Province, Denjai — 771-1	89.2	4.1	3.4	25.5	12.8	42.7	40.0	10.0	2.05
771-L									
Sisaket Province, Nam Awm — 149-1	87.3	3.3	3.3	27.2	13.3	19.7	56.7	12.9	0.68
149-2	70.3	4.4	17.9	5.8	27.7	24.0	49.3	14.7	0.88
150-1	84.9	1.0	1.1	83.0					
150-2	88.3	2.0	4.3	27.0					

"resilication" or similar phenomena in the course of development of the soil profile.

In considering table 2 it should be noted that almost the only soils in Thailand of which we can be reasonably certain that the parent materials are known, and which were even reasonably homogenous, are the very limited bodies of soils developed on some of the basic magmatic extrusions and on some of the limestone bluffs. In by far the greatest number of cases the parent materials of our soils are unknown. That this must be the case will be apparent when it is remembered that laterite soils, as well as lateritic and related soils, which we are considering in this paper, have developed either on a peneplain, which has usually cut across folded and faulted sedimentary and metamorphosed strata of diversified nature, or in an old stabilized alluvial plain. Even in the greater part of the Korat region, where the interbedded sandstones and shales appear to be only slightly disturbed, it is difficult to detect any close relationship between the character of the soils and the underlying rock even along extensive exposures in railway cuttings.

Another point to be kept in mind in considering the data in table 2 is that the method employed in crushing the sample preparatory to screening through the 2-mm. sieve was rather too vigorous. In several cases a considerable proportion of a sample of laterite has been crushed and has been treated as "fine earth"; consequently, the analyses of the softer portions of a number of laterite horizon samples appear in the analysis of the "fine earth." That this is so is evident from the fact that in at least some such cases the Fe/Al ratios of the "fine earth" are those we have found to be usual for laterite, and not of true fine earth associated with concretionary material of the laterite type.

Since the stages of development of the different profiles and samples are not

the same, and since some of the samples are gravelly loams in which the "gravels" are iron concretions, significant and useful comparisons of the analytical results presented herein are not always possible.

The silica/sesquioxide ratios of the "fine earth" are variable. It is evident that in some instances there has been considerable mechanical as well as chemical sorting of the finer fractions of the soil by eluviation and illuviation during the soil development process. And although it is doubtful whether they would give any definite measure of the degree of weathering, the silica/sesquioxide ratios of the colloidal clay of the different samples of laterite soils would also doubtless show interesting relationships.

Considering the data in table 2, group by group, according to the probable kind of parent materials from which the soils profiles have been derived, we find the following interesting relationships:

A—Parent materials probably derived from quartzitic sandstones. In the fine earth portions of the samples of this group the silica/sesquioxide ratios of the uppermost layers are very high, varying from 11 to 142. With increasing depth, these ratios are as a whole lower, chiefly because the clay has been carried down deeper into the soil. But in all cases in this group, even the deeper horizons have ratios above 1. There is often as much Al_2O_3 as Fe_2O_3, if not more.

By contrast, in the concretions, which in some instances constitute more than 80 per cent of the total sample, there is usually about five times as much Fe_2O_3 as Al_2O_3. Since considerable SiO_2 must be enclosed mechanically in both discrete concretions and in laterite, the percentages of SiO_2 in the concretions seem low in comparison with the very high proportion of SiO_2 in the total sample. These differences in composition of the fine earth and of the concretions are of the order of differences found by Beater (1) for tropical soils and are very much greater than those reported by Wheeting (19) for a temperate zone soil.

It is unfortunate that the phosphorus content of the concretions was not determined, for undoubtedly most of the small amounts of that element in the soil are locked up in these concretions. In the Philippines the senior author noted that the presence of such iron concretions in a soil was a certain indication that sugar cane growing on that soil would benefit from application of a fertilizer containing P.

In view of the diversity of the rocks and other materials that make up the parent materials, or perhaps because in most cases the parent materials are of such diversified composition and character, the silica/sesquioxide ratios in the concretions and in the laterites previously reported upon (15) have, with few exceptions, a remarkably similar trend.

B—Parent materials probably basaltic. There is little doubt as to the true character of the parent materials of the few samples in this group. In the samples from Trat Province it is notable that the analyses of the fine earth show closely similar quantities of Si, Fe, and Al down through the profile, though with depth there is an increase in the proportion of the sample made up of concretions, which usually contain considerably more Fe_2O_3 than Al_2O_3.

A comparison of the analyses of the parent rock and the overlying soil of

profile 151 indicates that there has been not only mechanical eluviation of the clay, but also considerable loss of Si in solution.

C—Parent materials probably limestone. Not only is there an outward similarity between the residual soils from limestone and from basalt, but in this group, as in the soils weathered from basaltic materials, the fine earth contains roughly twice the amount of Al_2O_3 as of Fe_2O_3. By contrast, in the concretions, which compose more than half the total sample of 544-M, there is twice as much Fe_2O_3 as Al_2O_3. Sample 354 is placed in this group because it is *probably* from limestone, since it resembles other soils seen in the vicinity of Taptieng, Trang Province, which appeared to be derived from limestone.

D—Parent materials probably mixed. This group of samples was collected from diverse locations in many different parts of Thailand. Some soils, like the five samples from Padang Besar, 308–313, are undoubtedly residual from a variety of more or less folded and metamorphosed sedimentary materials. It has been suggested that "accretions" might be a better term than concretions for the irregularly shaped, limonite-covered objects in these samples.

Other profiles of this group, such as 444, 576, 620, 633, and 634, have been developed in older or not so old, alluvia, while still other samples may have been derived from deeply weathered, older sedimentary formations.

It is interesting to note that the "fine earth" of many samples in this group contains 5 to 10 times as much Al_2O_3 as Fe_2O_3. On the other hand, in the concretions or laterite samples which were not broken up by the too vigorous preliminary crushing before sieving, there is two to five times as much Fe_2O_3 as Al_2O_3. That at times what has been analyzed as "fine earth" is definitely known to be actually broken up laterite is illustrated by sample 156-X, which was collected as a single solid, though fragile, quarried block from an old temple which had withstood the tropical weather for a thousand or more years (15).

As is usual with many of the samples reported in this paper, the soils in this group have a considerably higher proportion of Si in the surface than in the deeper horizons.

DISCUSSION OF TERMINOLOGY

"Podzolized," a much overworked expression

From the data in table 1 it is evident that many of the laterite or lateritic soils that have developed in a parent material high in quartz sand have a very much bleached, a very light brown, a cream-colored, or a dirty white, strongly acid eluvial horizon. In spite of the fact that the conditions which bring about the development of a laterite have never been known to produce the characteristic illuvial podzol horizon with its high content of organic matter, many North American pedologists (17, 18) insist upon calling the bleached horizon even of a laterite profile "podzolized."

Anyone who has had an opportunity to compare the striking differences between the illuvial horizons of typical podzols and of laterites should be convinced that *in addition to differences in scale there must be some basic difference or differences between the processes of podzolization and laterization.* Yet the

explanations of, and supposed causes for these differences, as stated by some authors (5, pp. 336–418; 18) appear of doubtful validity to us. Nevertheless, most of the factors, including the leaching and, in some instances, the bleaching of the eluvial laterite horizon do appear to be similar. If it were not that occasionally podzol profiles with their characteristic organic iron illuvial horizon have been observed in tropical lowlands (3; 12, p. 258), one might suspect that temperature was the determining factor, a lower temperature facilitating the precipitation of organic matter in podzols, and a higher temperature precluding it in laterites. But before satisfactory explanations of the reasons for the differences can be given, thorough studies of the two sorts of profiles and of all possible factors affecting their development must be made. In the meantime, it is very desirable to avoid applying the term "podzolized" to bleached or bleaching eluvial horizons that obviously belong to profiles in which a laterite horizon is developing. "Podzolized," "podzolic," and all similar adjectives should be limited to profiles which are distinctly developing toward a true podzol profile, with its characteristic coffee-colored iron–organic-matter illuvial horizon. In other words, the terms used for the parts of a profile should indicate an understanding of the general type of the profile as a whole and the direction in which the soil-forming processes appear to be trending. If laterite profiles were really becoming "podzolized," not merely having a bleached or paler lower eluvial horizon, certainly by this time we would have discovered at least some evidence of the characteristic podzol illuvial horizon developing in at least a few of our laterite soil profiles.

"Lixiviation" covers more than "podzolization" and "laterization"

"Lixiviation," as proposed by Mohr (8), is an appropriate term to cover the general process of the leaching downward of the elements liberated in the progressive hydrolysis of the rock minerals in the soil, a process which is especially important where percolation is predominant and considerable and where drainage is free. Soils that have been lixiviated or leached until the effects of the leaching are apparent are termed "lixivium soils." Suitable adjectives, usually indicating the colors of the horizons referred to, used with "lixivium" give expressions such as "gray lixivium," "yellowish lixivium," and "white lixivium," which convey a much clearer and more definite conception of the nature of the soil than such overworked and often misleading terms as "podzolic," "podzolized," and "laterized" or "lateritized" particularly when referring to laterite or lateritic soils. Light yellowish brown granular soils on the higher tropical mountains might be called "yellow mountain lixivium" or "yellow pseudosand lixivium" (8).

The character of the lixiviation must depend upon many factors, among which are (a) the physical nature and (b) the chemical composition of the parent rocks, particularly whether they are rich or poor in quartz, Ca, Mg, Fe, Al, Mn, etc.; (c) the kind and amount of the organic matter, which are governed by (d) the climate (the rainfall regime and the temperature), as well as by (e) the direction of movement of the water in the soil; and (f) the reaction of the solutes in the percolating water. But as long as most writers on these subjects are dependent on the more or less inadequate observations of others (10, 15) and hence have no

satisfactory means themselves of evaluating and weighing the uncertain and conflicting data, and in view of various and often conflicting conceptions as to what "laterization" and a "laterite profile" really are, it is not to be wondered that even the most recent definitions and discussions of these and related subjects (18) are disappointingly vague and conflicting. In the writings of American soil morphologists one frequently sees such expressions as "podzolized laterite soil." Such an expression seems to imply that one or more of the conditions have changed and that the environment which originally produced or had been producing a laterite profile has changed in some way, so that the environmental and internal factors now giving their impress to the profile are changing it from a lateritic type to or toward a podzol profile. We believe there will ultimately be found to be several types of lixiviation in soil developmental processes—certainly more than the one podzolic type! Particularly in soils rich in quartz sands, the "laterization process," in the strict sense of the term, will normally result in the eluvial horizon's being bleached virtually white, whereas under exactly the same climate and similar ground-water conditions a soil weathered from basic rock, that is, one containing no free quartz grains, will, with free drainage, seldom if ever show much bleaching. And since there are good reasons for believing that there are pronounced chemical differences between the podzol profile and the laterite profile, is not this alone an excellent reason for avoiding the use of the adjective "podzolized" in referring to a bleached horizon of a laterite profile?

Since, as yet, it appears impossible to draw up reasonably distinct and satisfactory definitions of "podzolizing," "lateritizing," and related terms, how much better it would be if the U. S. Soil Survey could take as liberal an attitude regarding such terms as "laterite," designating a soil type which is not known to occur in the continental United States (15), "laterization," and "podzolization" as it has taken with regard to "solonetz" (18, p. 977), designating a type which is much more accessible for study in the United States and about which there is not yet nearly so much confusion.

Laterization is a pedological process

To one accustomed to dealing with very thoroughly and deeply weathered equatorial soils, many temperate-zone profiles seem to be on a microscale. There seems no good reason to limit our pedological thinking to a depth of 1 or 2 m. merely because such a depth is often more than sufficient to include the entire profile of most temperate zone soils.

Without deep-rooted shrubs and trees growing on the land, the first meter of deeply weathered, senile equatorial soils may at times be virtually useless as a producer of annual crops (12, 14). Roots of perennial trees and shrubs can forage much deeper, even down into the zone where rock weathering is still progressing, there to get plant nutrients which may subsequently be used by shallow-rooted annual plants. Such plants would be able to use the decomposed offal of the trees or the plant nutrients liberated in the burning which is a part of the periodical caiñgining of the perennial forest cover crop (11).

It is difficult, if not impossible, properly to understand equatorial soils and

their fertility maintenance and effective utilization by natural and planted tree and annual crops without considering the entire profile, which is many meters deep in places.   And equatorial soil-forming processes affect a much greater

FIG. 1. COLLECTING SAMPLE 177 IN A TYPICAL FOREST ON LATERITE SOILS, 24 KM. NORTH OF KHON KAEN

To the left of the men and in the left foreground are heaps of laterite which have been dug out for road metalling, Khon Kaen Province, Northeastern Thailand.

FIG. 2. LIGHT GRAY GRAVELLY LOAM LATERITE SOIL ON WHICH PADI IS RAISED ANNUALLY

The gravels are iron concretions and at least in places there is a solid laterite horizon at about $\frac{1}{2}$ m. depth.   (Note the chunk of laterite against the padi dike in the left foreground.) The more luxuriant trees in the distance are growing on termite mounds.   Sakon Nakon Province, Northeastern Thailand

depth of materials making up the surface of the earth than do the temperate-zone soil-forming processes.

Nikiforoff may be taken as representing the other, the extreme temperate-zone point of view, when he says[4] that what he calls "straight line" processes

[4] C. C. Nikiforoff, in a personal conversation, September 1939.

Fig. 3. Light Yellowish Brown Light Fine Sandy Loam Lixivium Soil Only Recently
Cleared of Brush and Trees

The uppermost 15 cm. still much darkened by organic matter. South Thailand Agricultural Experiment Station Haadyai, Songkla Province, October, 1935

Fig. 4. Lateritic Soil Exposed by Erosion Following Excavation of Roadside
Borrow Pit

Note the irregular depth of the zone of dark iron concretions. In the right foreground an erosion pavement of these concretions has been exposed. The poor growth of the forest trees indicates that the soil is infertile. (See figure 5 for details of the profile.) Tatum
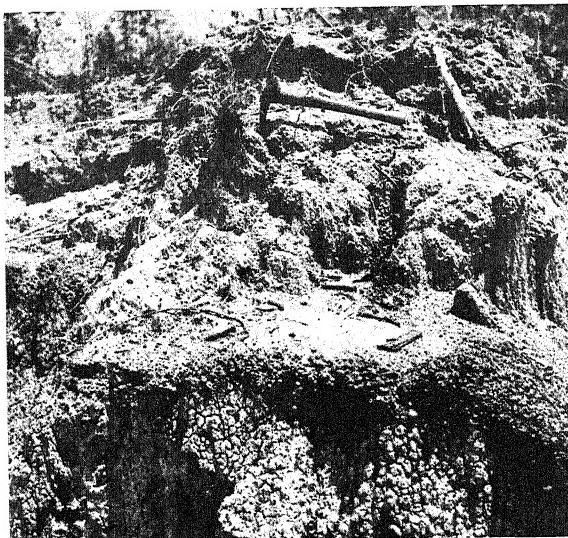
FIG. 5. DETAIL OF LATERITIC SOIL SHOWN IN FIGURE 4

Surface to the pick handle: Light brown fine lixivium sand. Pick handle to the partly cemented iron concretions: Light brown lixivium loam. The iron concretionary zone rests on the clay horizon.

Iron concretionary zone downward: Light bluish, gray and red clay, now cracked as a result of drying following exposure. Tatum township, Surin Province, Northeastern Thailand

FIG. 6. LATERITE HORIZON EXPOSED ON BANK OF ING RIVER

The bluish clay has been washed out from the tubules, leaving the reddish harder, ferruginous vesicular skeleton. It is still too soft to be quarryable. Above on the softer white lixivium soil lie quantities of dead leaves. Likely some of the uppermost portions of the profile, in the shadow of the brush, are more recent alluvial deposits. Sample 738-L, Terng Township, Chiengmai Province, Northern Thailand, December, 1938

which take place in the soil, such as leaching and almost all the weathering processes, should be considered geological processes, and that only those processes which have a smaller and more definitely closed or more obvious cycle,
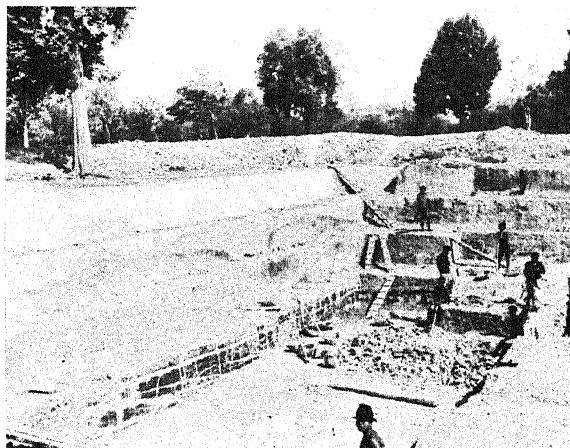
FIG. 7. EXCELLENT PROFILE OF A LATERITIC SOIL EXPOSED BY EXCAVATION FOR WATER-STORAGE POND AT BAN TAM YAE, UTUMPON TOWNSHIP, UBON PROVINCE, NORTHEASTERN THAILAND

The topmost terrace slope exposes the surface light pinkish gray light very fine sandy loam. The dark horizon on the second terrace, at variable depth, is made up of limonite-coated iron concretions, just above which is a horizon of finely mottled light pinkish gray, light brown, and brown gravelly clay loam, the gravels being iron concretions. At the bottom is exposed the dark purplish red soft Tertiary sandstone, which is the principal parent material of the soils of the Korat region. The light bluish white streaks in the sandstone are due to weathering that has taken place along the joint planes and cracks of the rock.

FIG. 8. THE PICK LIES ON AN EROSION PAVEMENT COMPOSED OF LOOSE LIMONITIC CONCRETIONS. SOME LARGER MASSES OF COALESCED CONCRETIONS, FORMING PISOLITIC LATERITE ARE IN THE FOREGROUND

The surface soil which had been eroded was a light pinkish brown light fine sandy loam. Möang township, Ubon Province, Northeastern Thailand

such as organic matter transformations, should be considered pedologic. Nevertheless, since obviously both sorts of processes are really cyclic, it seems more logical to consider pedologic all those weathering or other alteration processes taking place in the surface crust of the earth which involve transformations of material and result in the development of the soil profile, including laterite formation and various types of pan formation, whether such transformations are going on within a few centimeters of the soil surface or one or a number of meters below it.

But even if it be admitted, on certain grounds, that deep weathering in equatorial or tropical regions might more properly fall within the scope of geology, a more important reason for stretching a point, if that be thought necessary, to include the deeper weathering processes and products within the scope of pedology is that geologists, as Marbut has said plainly (6), do not seem to be interested in the soil development processes and do not appear to be helping much in the clarification of pedological problems. If we leave the working out of such questions to the geologists, we will not be apt to get much help, for neither the training nor the interests of geologists are along pedological lines.[5] As a whole, geologists have often beclouded the issue (4) or have quite neglected to give data which are essential for an adequate understanding of the whole soil profile (2).

If we, as pedologists, do not understand the nature of these weathering processes or what may be the nature of the end products, how can we be in a position to understand fully the character of the soil developmental problems and the nature of the final products? It is much better to be a little more inclusive in the scope of pedology and to try to understand those processes, than merely to call laterite and other secondary formations in the profile "soil parent materials" and let it go at that.

Because laterite is a deposit of highly oxidized iron compounds—an end product of the most rigorous soil weathering process known, resulting from abundant moisture and the oxidizing conditions that prevail at the earth's surface in humid equatorial regions—it certainly can *not* be considered a parent material for soil formation. Laterite is "the bones of a dead soil" (8). It is for these reasons that under a climate where frost never occurs, laterite is extremely resistant to equatorial weathering processes. Laterite believed to have been developed in Tertiary times still caps hills in central India (9), and the senior author has shown (13) how resistant laterite in structures is to subaerial tropical weather.

SUMMARY AND CONCLUSIONS

A new approach in studying equatorial soils is needed. Until we can make a fresh approach it seems impossible to resolve the prevailing confusion and misleading ideas regarding equatorial soils, especially with regard to the nature and manner of formation of laterite and laterite soils.

Profile descriptions and chemical analyses of samples of laterite soils and some

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[5] With regard to laterite, the outstanding exception is J. Morrow Campbell, a mining engineer.

related soils collected from many widely separated localities in Thailand have been presented. "Laterite" is used in the strict original sense of Buchanan: an iron-oxide-rich, indurated, quarryable slag-like or pisolitic illuvial horizon developed in the soil profile.

In soil survey work field-applicable criteria for evaluating soils are essential. Laterite or other lateritic horizons are easily distinguished in the field, and since laterite soils are infertile, the presence or absence of laterite in a soil is an important criterion of soil character.

The fine earth and concretionary materials of the samples studied were separately analyzed by the fusion method. When the physical separations are carefully made the proportions of iron and aluminum in the concretionary materials differ markedly from those in the fine earth.

The total amount of sesquioxides which can accumulate in the soil depends upon the proportions in the original parent materials, as well as upon horizontal movements of sesquioxides which may have occurred in the ground water to and from the profile in question. Under most conditions the percentage of concretionary material (including laterite) in laterite soils and lateritic soils likely indicates the degree of weathering better than the silica/sesquioxide ratios in the colloidal clay.

The percentages of silica in the fine earth and in the laterite and concretions appear to be affected to a considerable degree by the inclusion of silica physically as matrix material. "Resilication" is not likely an important factor in laterite soil profile development.

When the results of the analyses are grouped according to the probable nature of the parent materials from which the profiles were derived, the following relationships may be noted:

A—Parent materials probably from quartzitic sandstones: 1. In the fine earth, marked mechanical eluviation is apparent. Silica/sesquioxide ratios, particularly of the surface horizons, are high. In many samples, the Al_2O_3 is equal to or greater than the Fe_2O_3. 2. In the concretions and/or laterite there is usually about five times as much Fe_2O_3 as Al_2O_3.

B—Parent materials basaltic: 1. No marked mechanical eluviation is evident in the fine earth profiles. Silica/sesquioxide ratios are low and relatively uniform; there is about twice as much Al_2O_3 as Fe_2O_3. 2. In the concretions and/or laterite the silica/sesquioxide ratios are less than 1. There is, roughly, twice as much Fe_2O_3 as Al_2O_3.

C—Parent materials probably limestone: 1. In the fine earth the silica/sesquioxide ratios are 2 or less; Al_2O_3 is 3 to 10 times as abundant as Fe_2O_3. 2. In the concretions the silica/sesquioxide ratios are less than 1; there is usually about twice as much Fe_2O_3 as Al_2O_3.

D—Parent materials probably of mixed alluvial origin: 1. In the fine earth the silica/sesquioxide ratios are generally high, particularly in the surface horizons, and there is usually 2 to 10 times as much Al_2O_3 as Fe_2O_3. 2. In the concretions and/or laterite the silica/sesquioxide ratios are low, though more variable than in some other groups. There is commonly about 3 times, and in many cases 5 times, as much Fe_2O_3 as Al_2O_3.

Laterite soil profiles developed in materials high in quartz usually have well-bleached eluvial horizons, whereas those developed from basic rock materials have red eluvial horizons.

As compared with the laterite profile, a podzol profile, besides being on a

microscale, must have been formed by a leaching process distinct in some manner from that which produced a laterite. Therefore, "podzolized" is not an appropriate adjective to apply to any horizon of a laterite soil. "Podzolized," "podzolic," and related terms should be used only in reference to a true podzol profile.

"Lixiviation" is a more suitable and less ambiguous term to designate all leaching processes in the soil. Further clarity as to the character of the horizon referred to will be gained by combining the term "lixivium" with the appropriate term to indicate the color of the horizon leached.

Laterization, the process which brings about the development of a laterite profile, should be considered within the scope of pedology, even though the profile of a laterite may extend far below the usually designated limits of an agricultural soil profile.

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DETERMINATION OF SILICA AND PHOSPHORIC ACID IN SOIL EXTRACTS[1]

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During the course of an investigation on the mode of action of colloidal silica in increasing the availability of soil phosphorus to cereal crops (25, 26, 27), some difficulties were encountered in the application of the Pemberton–Kilgore titrimetric method (8, 11, 17, 18, 19, 21) for determining phosphates in soil extracts containing appreciable amounts of silica in solution. Some previous workers (9, 10, 16, 20) have shown that the presence of soluble silica does not interfere with this method of estimation, whereas others (2, 12, 21, 22) have found interference due to silica.

In one set of experiments, therefore, equal volumes of a standard solution of potassium dihydrogen phosphate (A. R.) were treated with different known amounts of a solution of sodium silicate, and the phosphate in the mixture was estimated by the usual official method (1). The results are shown in table 1.

It was observed that, with small concentrations of silica, the values for phosphate in solution were but slightly affected, but the precipitate was greenish-yellow, flocculent, difficult to filter, and very slow to dissolve in the alkali [cf. (28)]. Larger amounts also caused very slow filtration and difficulty in washing and, besides, gave higher results, probably because of the formation of silicomolybdic acid (13, 21). In many of these cases, the filtrate was also colored yellow. To obtain correct values, it was therefore felt necessary to remove silica from solution completely.

REMOVAL OF SILICA FROM SOLUTION

Silica is generally removed from solution by acidification, evaporation, dehydration, and filtration. Repetition of this process is necessary for complete separation of silica (1). The method is tedious and time-consuming. Moreover, it was thought that repeated evaporation to complete dryness of soil extracts containing phosphate, iron, and aluminum might reduce the quantities of phosphate finally found in solution. Consequently, some attempts were made to separate silica completely from solution by the use of dehydrants in place of evaporation. Several experiments were carried out with sulfuric acid,

perchloric acid, and chromic anhydride, and it was found that the following procedure was not only expeditious but gave the most satisfactory results:

The solution containing the phosphate is evaporated to a small bulk on the water bath, then treated with 5 cc. of concentrated (preferably fuming) sulfuric acid, followed by 5 to 10 cc. of alcohol, and left on the water bath for about 15 minutes, when the silica separates in fine granules. The mixture is then diluted with water and left on the water bath for another 15 minutes before being filtered. The precipitate is washed free of acid, ignited, and weighed as SiO_2.

It was found that with this method the silica from known amounts of a standard solution of sodium silicate could be recovered quantitatively. The results are presented in table 2.

TABLE 1

Determination of phosphate in solution in presence of soluble silica

SOLUBLE SODIUM SILICATE ADDED	PHOSPHATE*, AS STANDARD 0.05 N ALKALI CONSUMED IN TITRATION		
	Replicates		
mgm. SiO₂	cc.	cc.	cc.
25	42.6	43.5	41.9
50	41.8	44.0	39.2
75	43.4	44.0	†
125	46.6	†	†
250	44.9	†	†

* Expected = 42.8 cc.
† Filtration very slow.

TABLE 2

Recovery of silica from solution

Silicate present.....................mgm. SiO_2	30	61	121	242	363	484
Silicate recovered..................mgm. SiO_2	30	59	124	237	349	469

The alcohol produces fine division of the precipitate and thus hastens the filtration. It abstracts water from the colloidal hydrated silica and thus causes it to precipitate quantitatively. Careful heating of the mixture of sulfuric acid and soil extract over a flame also increases the rate of filtration. Starting with about 100 cc. of solution, the whole operation can be completed in less than $1\frac{1}{2}$ hours.

DETERMINATION OF SILICA AND PHOSPHATE IN A SOLUTION CONTAINING A MIXTURE OF THE TWO

Known amounts of standard solutions of potassium dihydrogen phosphate and sodium silicate were mixed together. From the mixtures thus obtained, the silica was separated by the foregoing method, and the phosphate in the filtrate and washings (about 100 cc. in all) was determined titrimetrically after

neutralization of the acid with ammonia and precipitation with the molybdate reagent at 40°–45°C. together with overnight standing (28). A few typical results are given in table 3.

It may be seen that fairly accurate results, both for the silica and for the phosphate in solution, are obtained by this procedure.

RAPID DETERMINATION OF SILICA AND PHOSPHORIC ACID IN SOIL EXTRACTS: MODIFIED NEUMANN'S METHOD FOR PHOSPHATE DETERMINATIONS

In determining phosphate by the Pemberton method as above, the precipitation had to be done at a low temperature (40°C.) and the mixture allowed to stand overnight. Besides, the molybdate reagent had to be prepared afresh every now and then, as, otherwise, molybdic oxide tended to separate and make the reagent weak. Furthermore, it was necessary, in view of the interfering action of sulfuric acid and of sulfates except ammonium sulfate (28), to

TABLE 3

Determination of phosphate and silicate in a mixture of the two in solution

MIXTURE	PHOSPHATE, AS STANDARD 0.05 N ALKALI CONSUMED IN TITRATION		SILICATE	
	Expected	Found	Expected	Found
	cc.	*cc.*	*mgm. SiO₂*	*mgm. SiO₂*
1	10.7	10.8	121	112
2	21.4	21.8	121	115
3	42.8	41.9	121	109
4	21.4	22.0	242	212
5	42.8	43.0	484	469
6	85.6	84.2	484	472

neutralize the sulfuric acid used for removing silica from solution before addition of the molybdate reagent. Such a procedure was tedious and time-consuming.

The Neumann method (14, 15) for determining phosphorus in organic matter is based on the oxidation of the material by a mixture of concentrated sulfuric and nitric acids, precipitation of the phosphate in the presence of ammonium nitrate with aqueous ammonium molybdate solution at a temperature near the boiling point of the mixture, and titration of the precipitate with standard alkali as usual. According to this procedure, the phosphate is precipitated as a phosphomolybdate–sulfate complex for which the conversion factor, 1 cc. of normal alkali = 2.536 mgm. of P_2O_5, is used. The composition of the precipitate is thus different from that obtained by the Pemberton procedure.

Since in the experiments on the estimation of phosphate in the presence of silica, sulfuric acid had to be employed for the separation of the latter, it was thought that the phosphate in the filtrate could be estimated directly by the Neumann method without neutralization of the sulfuric acid with ammonia.

After a few trials with mixtures of known composition, the following method was found to work very satisfactorily:

The solution is evaporated to a small bulk (5 to 10 cc.). The silica is separated by dehydration with sulfuric acid and alcohol as previously described. The filtrate and washings (about 100 cc. in all) are treated with 20 gm. of ammonium nitrate and heated almost to boiling over a flame. Then 20 cc. of a 10 per cent aqueous solution of ammonium molybdate is added, followed by vigorous stirring. The mixture is left at about 80°C. for approximately 15 minutes. The yellow precipitate is then filtered off, washed with cold or, preferably, hot water until free from acid, and titrated in the usual way. The phosphate present is calculated by use of the Neumann factor: 1 cc. of normal alkali = 2.536 mgm. of P_2O_5.

TABLE 4

Determination of phosphate and silica in presence of soil-water extracts

PHOSPHATE		SILICATE	
Added	Found	Added	Found
mgm. P_2O_5	*mgm. P_2O_5*	*mgm. SiO_2*	*mgm. SiO_2*
Red loam soil			
0	0	0	2
1.96	2.00	121	119
1.96	1.94	242	225
3.92	3.90	121	109
3.92	3.79	242	220
7.84	7.76	484	480
Heavy clay soil			
0	tr.	0	6
1.96	1.98	61	62
3.92	3.85	121	118
3.92	3.88	242	234
5.88	5.97	0	4

This procedure for phosphate determination was found to be more satisfactory than the Pemberton method. The operations could be carried out much more quickly, the washings could be done with water instead of with dilute nitrate solution, and slight changes in the volume or in the temperature of precipitation did not affect the accuracy of the results. Silica in solution, however, gave high results and had to be removed before determination of the phosphate. High concentrations of alkali sulfates also interfered with the method, low values being obtained in these cases.

In a series of experiments, 50-cc. lots of a 1:1 soil–water extract from a red loam and a heavy clay soil, respectively, were mixed with varying known amounts of phosphate and silicate in solution. The quantities of the latter as determined by the foregoing procedure are given in table 4.

The method is thus seen to work in the presence of soil-water extracts.   Similar results were obtained on 50-cc. lots of soil–acid extracts (table 5).

Some experiments were also carried out on a light clay soil treated in 50-gm. lots with the same amount (10 mgm. P_2O_5) of a standard solution of KH_2PO_4.

TABLE 5

Determination of phosphate and silica in presence of soil-acid extracts
Red loam soil

EXTRACTANT	PHOSPHATE		SILICATE	
	Added	Found	Added	Found
	mgm. P_2O_5	*mgm. P_2O_5*	*mgm. SiO_2*	*mgm. SiO_2*
Citric acid (1 per cent)........................	0	tr.	0	6
	1.96	1.88	61	63
	1.96	1.90	121	118
Acetic acid (1 per cent)........................	0	0	0	4
	1.96	1.92	121	117
	3.92	3.80	242	229
Sulfuric acid (0.2 N)........................	0	0	0	4
	1.96	1.94	121	124
	3.92	3.88	242	224
Hydrochloric acid (1 per cent).................	0	tr.	0	6
	3.92	3.79	121	118
Nitric acid (1 per cent).......................	0	tr.	0	6
	1.96	1.90	484	468
	5.88	5.69	121	119

TABLE 6

Recovery of added phosphate by different extractants

EXTRACTANT	PHOSPHATE RECOVERED	
	Official method (1)	Modified method
	mgm. P_2O_5	*mgm. P_2O_5*
Dyer's 1 per cent citric acid (4, 5)............................	2.53	2.61
Frap's 0.2 N nitric acid (7).................................	2.10	2.13
Truog's 0.002 N sulfuric acid buffered to pH 3 with ammonium sulfate (29)...	6.50	6.46
Das's 1 per cent potassium carbonate (3).....................	3.60	3.48
Egner's calcium lactate-hydrochloric acid (6).................	2.00	1.96

The amounts of phosphate brought into solution by several of the common extractants [cf. (23)] were determined by both the official and the modified methods.   The results are given in table 6.

In other experiments, 50-gm. lots of the red loam soil were treated with

different known quantities of a solution of sodium silicate followed by known amounts of a solution of phosphate. The mixtures were allowed to stand for about half an hour, after which they were extracted by shaking in an end-over-end shaker for 2 hours with 200 cc. of water. The quantities of silica and phosphate in aliquots of the extracts were then determined in each case by the official and modified methods. The results are shown in table 7. The very poor recovery of added silicate and phosphate, especially at low concentrations, undoubtedly is due to their retention by the soil colloids (25, 27).

It may thus be seen that the method of dehydration of silica by sulfuric acid followed by the determination of phosphate by the Neumann procedure can be successfully adopted in studies with soil and with soil–water or soil–acid extracts under different conditions. The method is particularly advantageous and rapid in studies on the influence of colloidal forms of silica in increasing phosphorus resorption from soils by cereal crops (24). It is possible, however, that in aqueous soil extracts containing only small quantities of silica and phosphate, the official Pemberton method or the molybdenum-blue colorimetric method may be more satisfactory for determining phosphate in solution.

TABLE 7

Recovery of added silicate and phosphate from solution

Silicate added.............................$mgm.$ SiO_2	0	242	242	484
Silicate extracted, Official................$mgm.$ SiO_2	5	91	88	248
Silicate extracted, Modified...............$mgm.$ SiO_2	4	4	85	226
Phosphate added..........................$mgm.$ P_2O_5	0	1.96	3.92	7.84
Phosphate extracted, Official...............$mgm.$ P_2O_5	0	0.52	1.64	2.85
Phosphate extracted, Modified.............$mgm.$ P_2O_5	0	0.49	1.58	2.73

SUMMARY

A rapid method for separating silica from soil extracts quantitatively by evaporation to small volume and digestion with sulfuric acid and alcohol has been worked out, and a quick and satisfactory procedure for determining silica and phosphoric acid in the same aliquot of soil extracts is described. The silica, after precipitation, is filtered off and the phosphate in the filtrate is determined titrimetrically by a modification of Neumann's method.

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THE ELECTRICAL CAPACITY OF THE 2-ELECTRODE PLASTER OF PARIS BLOCK AS AN INDICATOR OF SOIL-MOISTURE CONTENT

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The practicability of the electrical resistance of the 2-electrode plaster of paris block as an indicator of the moisture content of soil in which plants are growing has been demonstrated (1, 2). Another electrical property of the same 2-electrode plaster of paris block shows excellent promise as an indicator of soil-moisture content. This is its *electrical capacity*, C, which is the quantity of electricity either of the electrodes will hold when there is unit potential difference between the two electrodes.

The electrical capacity depends greatly on the medium between the electrodes. If we let C_O represent the capacity when the electrodes are entirely surrounded by a vacuum or by air, then the capacity of the electrodes when they are immersed in some other medium is given by

$$C = D \, C_O \qquad (1)$$

where D is the dielectric constant of the medium. It will have a different value for each medium. What interests us most here, as has already been pointed out (3), is that such substances as water have a very high dielectric constant ($D = 80$ approximately) whereas such substances as dry soil have a very low dielectric constant ($D = 5$ approximately) and moist soil a dielectric constant intermediate between the two, the magnitude of D increasing with the amount of moisture present in the medium. According to equation (1), therefore, the electrical capacity of the condenser composed of the two electrodes immersed in the medium will be low when the medium is dry, and high, when the medium is moist. The capacity, C, should therefore serve as an indicator of the moisture content of the medium surrounding the electrodes.

To test the practicability of the electrical capacity of the plaster of paris blocks as an indicator of soil-moisture content, answers to the following questions must be obtained:

How reproducible are the measurements made by this method? For example, suppose we find at a moisture content near the permanent wilting percentage of the soil that the capacity of the blocks is 0.006 microfarad. Then suppose after irrigating the soil one or more times we again determine the soil-moisture content and the capacity and find the latter to be 0.006 microfarad. How close will the value of the soil-moisture content in the latter case be to the former? If the difference is too great, obviously the method is useless as a soil-moisture content indicator.

Also, suppose we find that the method gives reproducible results under certain

conditions.   How much time must be allowed for the block to establish a moisture-content equilibrium with the soil surrounding it?   It is well known that, particularly at the lower moisture contents, moisture moves more slowly, the lower is the moisture content.   If it moves too slowly, a plant may die long before the instrument indicates that the soil has reached the permanent wilting percentage.

And finally, how much is the electrical capacity of the block changed by a change in the separation of the electrodes?   The answer to that question is important, for the less the change in capacity, the less care is required in the proper spacing of the electrodes to ensure comparable results from the blocks, and therefore, the lower is the cost of manufacture of the blocks.

APPARATUS AND PREPARATION OF THE PLASTER OF PARIS BLOCKS

The plaster of paris blocks and the Wheatstone bridge circuit used for determining the electrical capacity of the blocks have been described in detail elsewhere (1).   For the variable condenser C_3 in one of the arms (fig. 1), a 4-decade capacitor was used having a range of electrical capacity extending from 0.0001 to 1.0 microfarad in steps of 0.0001 microfarad.

The expression used in calculating the electrical capacity C_4 of the 2-electrode plaster of paris block from the settings of the Wheatstone bridge is given by the following equation[1]

$$C_4 = \frac{R_1}{R_2} C_3 \tag{2}$$

[1] Whether used to determine resistance or the capacity, the bridge is balanced the same way.   In both cases we must obtain a balance not only in the resistances but also in the capacities of the bridge.   When the bridge is balanced with respect to resistance only, it will be recalled that

$$\frac{R_1}{R_2} = \frac{R_3}{R_4} \tag{3}$$

Now, designating the currents as indicated in figure 1, we have

$$i_1 = i_3 + i_5 \tag{4}$$

$$i_2 = i_4 + i_6 \tag{5}$$

$$R_1 i_1 = R_2 i_2 \tag{6}$$

$$R_3 i_3 = R_4 i_4 \tag{7}$$

$$\frac{1}{C_3} \int_0^t i_5 \, dt = R_3 i_3 \tag{8}$$

$$\frac{1}{C_4} \int_0^t i_6 \, dt = R_4 i_4 \tag{9}$$

Eliminating i_5 between equations (4) and (8) and i_6 between equations (5) and (9) results in

$$i_1 = i_3 + C_3 R_3 \frac{di_3}{dt} \tag{10}$$

$$i_2 = i_4 + C_4 R_4 \frac{di_4}{dt} \tag{11}$$

Substituting in equation (11) the values of i_2 and i_4 from equations (6) and (7) and elimi-

No new operations are involved in the determination of the electrical capacity of the plaster of paris block that were not involved in the determination of the electrical resistance of the block. We merely use equation (2) instead of equation (3).

REPRODUCIBILITY IN BEHAVIOR OF THE BLOCK CAPACITY

Laboratory studies

A detailed account of the present experimental procedure will be found elsewhere (1), since the investigations of the use of both the electrical capacity and the electrical resistance of plaster of paris blocks as an indicator of soil-moisture content were carried on simultaneously.

The plaster of paris blocks were imbedded in buckets, each containing approximately 11 kgm. of dry soil in which several sunflowers (which served to change continuously the moisture content of the soil surrounding the blocks)
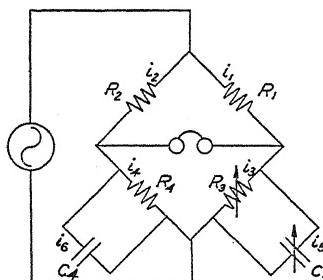
FIG. 1. WHEATSTONE BRIDGE CIRCUIT USED IN DETERMINING THE ELECTRICAL CAPACITY OF THE PLASTER OF PARIS BLOCK

R_1 and R_2 represent the resistances of the ratio arms; C_3 and R_3, the capacity and the resistance of the third arm; C_4 and R_4, those of the plaster of paris block; and the i's, the currents in the parts indicated

were growing. Each cycle of events commencing with an irrigation in which the soil is saturated and ending with the soil at the permanent wilting percentage makes it possible to plot a curve showing the dependence of the capacity of a given block on soil-moisture content. The degree of coincidence of the curves, each obtained from a different cycle, is a reliable indication of the reproducibility in behavior as well as of the amount of reliance that can be placed on the blocks as indicators of soil-moisture content in soils in which plants are growing.

To provide an indication of the lag in response of the blocks to changes of

nating i_1 between the resulting equation and equation (10) we have

$$i_3 + C_3 R_3 \frac{di_3}{dt} = \frac{R_2 R_3}{R_1 R_4} i_3 + C_4 R_3 \frac{R_2}{R_1} \frac{di_3}{dt} \tag{12}$$

Imposing on this, equation (3) (the condition for the balance of the resistance only), we have equation (2).

moisture content, the average rate of transpiration of the sunflowers was varied from one cycle to the next, as described elsewhere (1).

If the blocks show such a lag, it is evident that the curve for any given cycle (showing the dependence of block capacity on soil-moisture content) should fall higher in the graph, the more rapid is the rate of transpiration during that cycle. That there is a surprising absence of lag in response is evident from the curves in figure 2-P. The points of each curve represent the data from at least five or six cycles of complete soil saturation and drying out by the roots of actively transpiring plants. Each point is labeled according to the cycle in which it was obtained. The cycles shown in the figure begin with the fifth, because the present investigations were carried out simultaneously with those on the electrical resistance of the plaster of paris blocks and because it was not until the end of the fourth cycle that a condenser suitable for accurate capacity determinations was obtained. The results with six blocks are plotted in figure 2-P, the origin of the ordinate of each curve being displaced vertically as indicated by the staggered logarithmic scales.

The moisture equivalent and permanent wilting percentage of the soil are indicated by two vertical lines, showing that the major variation in the capacity of the block is distributed continuously over the entire range of readily available moisture content to plants. The electrical capacity corresponding to the permanent wilting percentage is approximately 0.00015 microfarad and that corresponding to the moisture equivalent, about 0.10 microfarad.

The curves of figure 2-P are all seemingly horizontal from the moisture equivalent to several times this value. The soil-moisture content at the beginning of the horizontal part of the curve doubtless corresponds to the minimum at which all the pores of the block are entirely filled. When this point is reached, additional water applied to the soil cannot alter the observed electrical properties of the block in the soil, since the block is the locale of virtually all lines of electric force between the electrodes (1). Below the moisture equivalent, the capacity decreases rapidly with decrease of soil-moisture content until it reaches a very low, seemingly constant, value a little above the permanent wilting percentage.

A comparison of the curves of figure 2-P, obtained from electrodes separated by 2.0 cm., with those of figure 2-Q, obtained from electrodes separated by 4.0 cm. in the same blocks, shows no outstanding difference.

Theoretical considerations also support the fact that the dependence of the capacity of the 2-electrode plaster of paris block on the separation of the electrodes is relatively small. The electrical capacity C per unit length of two straight parallel cylindrical electrodes (6), of radius a, placed with their centers at a distance ρ apart in an infinite medium, the dielectric constant of which is D, may be expressed as follows:

$$C = \frac{D}{4 \cosh^{-1}\left(\frac{\rho}{2a}\right)} = \frac{0.109D}{\log_{10}\left\{\frac{\rho}{2a} + \left(\frac{\rho^2}{4a^2} - 1\right)^{\frac{1}{2}}\right\}} \text{ cm.} \qquad (13)$$
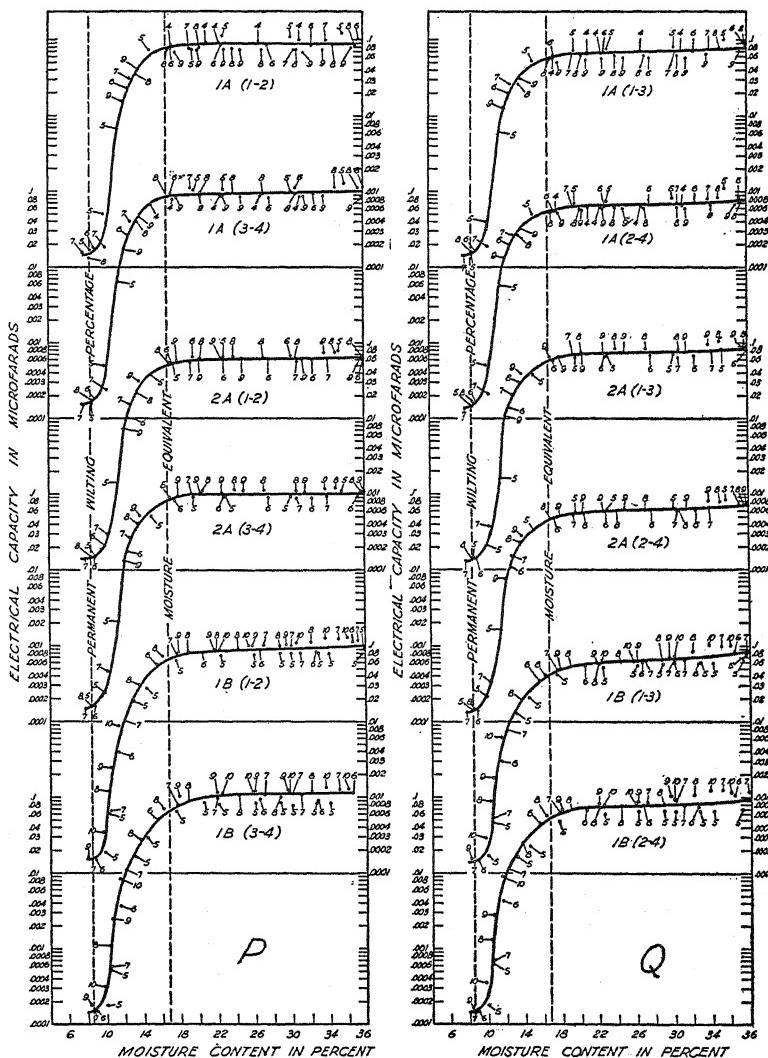
FIG. 2. DEPENDENCE OF ELECTRICAL CAPACITY OF 12 PLASTER OF PARIS BLOCKS ON MOISTURE CONTENT OF YOLO FINE SANDY LOAM, ACCORDING TO LABORATORY STUDIES

The left side, *P*, refers to blocks in which the electrodes are 2.0 cm. apart; the right side, *Q*, to blocks in which the electrodes are 4.0 cm. apart. Staggered vertical logarithmic scales indicate a vertical displacement of the origins of adjacent curves by 1000 ohms. The number attached to each point indicates the number of the cycle during which the point was obtained. Each curve is the results of five or six cycles of complete soil saturation and drying caused by growing plants.

When the electrodes are at a great distance ρ apart compared to their radius a, as is approximately true in the case of the 2-electrode plaster of paris blocks, equation (13) reduces to

$$C = \frac{0.109D}{\log_{10}\left(\dfrac{\rho}{a}\right)} \qquad (14)$$

If the separation of the electrodes is changed from ρ_1 to ρ_2, we can set

$$\rho_2 = k\rho_1 \qquad (15)$$

where k is merely a number such as to satisfy equation (15). From equations (14) and (15) the following expression is obtained for the percentage change in the electrical capacity of the plaster of paris blocks caused by changing the separation of the electrodes from ρ_1 to ρ_2

$$\frac{\Delta C}{C} 100 = \frac{C_2 - C_1}{C_1} 100 = \frac{\log_{10} k}{\log_{10}\left(\dfrac{\rho_2}{a}\right)} \qquad (16)$$

If the separation of the electrodes is doubled, from $\rho_1 = 2.0$ cm., corresponding to figure 2-P, to $\rho_2 = 4.0$ cm., corresponding to figure 2-Q, and $a = 0.032$ cm., then $k = 2$, and equation (16) becomes

$$\frac{\Delta C}{C} 100 = -14.3 \text{ per cent.}$$

This is approximately how much less all the capacities of figure 2-Q are than those of figure 2-P.

Let us apply equation (16) to the practical case of finding what change in the capacity of the 2-electrode block is caused by the error of placing the electrodes 2.3 cm. instead of 2.0 cm. apart. From equation (15), $k = 1.15$, and the change in the capacity caused by the error would be

$$\frac{\Delta C}{C} 100 = -3.3 \text{ per cent}$$

Had the electrodes accidently been placed 1.7 cm. instead of 2.0 cm. apart, $k = 0.85$ and the change would be

$$\frac{\Delta C}{C} 100 = 4.1 \text{ per cent}$$

Thus an error of 15 per cent in the separation of the electrodes during the casting of the blocks should cause a deviation of only about 4 per cent in the capacity readings of the blocks. These theoretical considerations show that for all practical purposes not an excessive amount of care need be exercised in the spacing of the electrodes in the midplane of the block so long as their separation is about 2 cm.

Field studies

The present field investigations of the dependence of the electrical capacity of the plaster of paris blocks on the moisture content were carried out on the same blocks, simultaneously with field investigations, to be reported in the future, of the dependence of the electrical resistance of the blocks on the moisture content of the surrounding soil. A more detailed account of the present experimental procedure will therefore be given later. The separation of the electrodes in all the blocks, the results of which are reported in the following, was 2.0 cm.

Figure 3 shows the results for six plaster of paris blocks all placed at the 18-inch depth in a sugar beet field of Yolo clay. The left side presents a history of both the moisture content and the electrical capacity throughout the season and shows two complete cycles, each commencing with a thorough irrigation followed by a drying out of the soil by the sugar beets. The set of curves on the right showing the dependence of the capacity of the block on its moisture content are derived from the curves on the left by plotting simultaneous values taken at approximately 5-day intervals. Because of the stickiness of the soil, no soil samples were taken at moisture contents higher than those indicated.

Figure 4 was obtained from measurements on blocks all placed at the 18-inch depth in a sudan grass plot of Yolo fine sandy loam. The results of three partial cycles are shown. The first is very short, because of irrigation difficulties. The other two are more complete.

Figure 5 was obtained from measurements on blocks all placed at the 18-inch depth in a sugar beet field of Yolo sand. The results from three complete cycles are shown.

The curves on the right of figures 3, 4, and 5 show the reproducibility and absence of lag in response of the electrical capacity of the plaster of paris blocks to be expected under field conditions for three soils of widely different texture. They all show that the blocks have a very high capacity (approximately 0.070 microfarad) in the vicinity of the moisture equivalent. With decrease of soil-moisture content below the moisture equivalent, the capacity falls, approaching a very small but constant value (approximately 0.00035 microfarad) in the vicinity of the permanent wilting percentage.

It is important that the blocks be placed in the soil, where plants are already growing, far enough in advance of their use as soil-moisture content indicators so that the roots will have had time to spread uniformly throughout the region of the soil immediately surrounding the blocks. A disregard of this precaution explains the divergence of the dotted top right curves for two of the blocks of figure 5, representing the first cycle, from that for the second and third cycles. During the greater part of the first cycle, the moisture content of the soil (average moisture content of the main body of the soil is represented by the abscissa in the figure) immediately surrounding the block, and therefore the capacity of the block, remained constant as a result of the absence of roots in the immediate vicinity of the block. Thus we find the electrical capacity continuing to remain
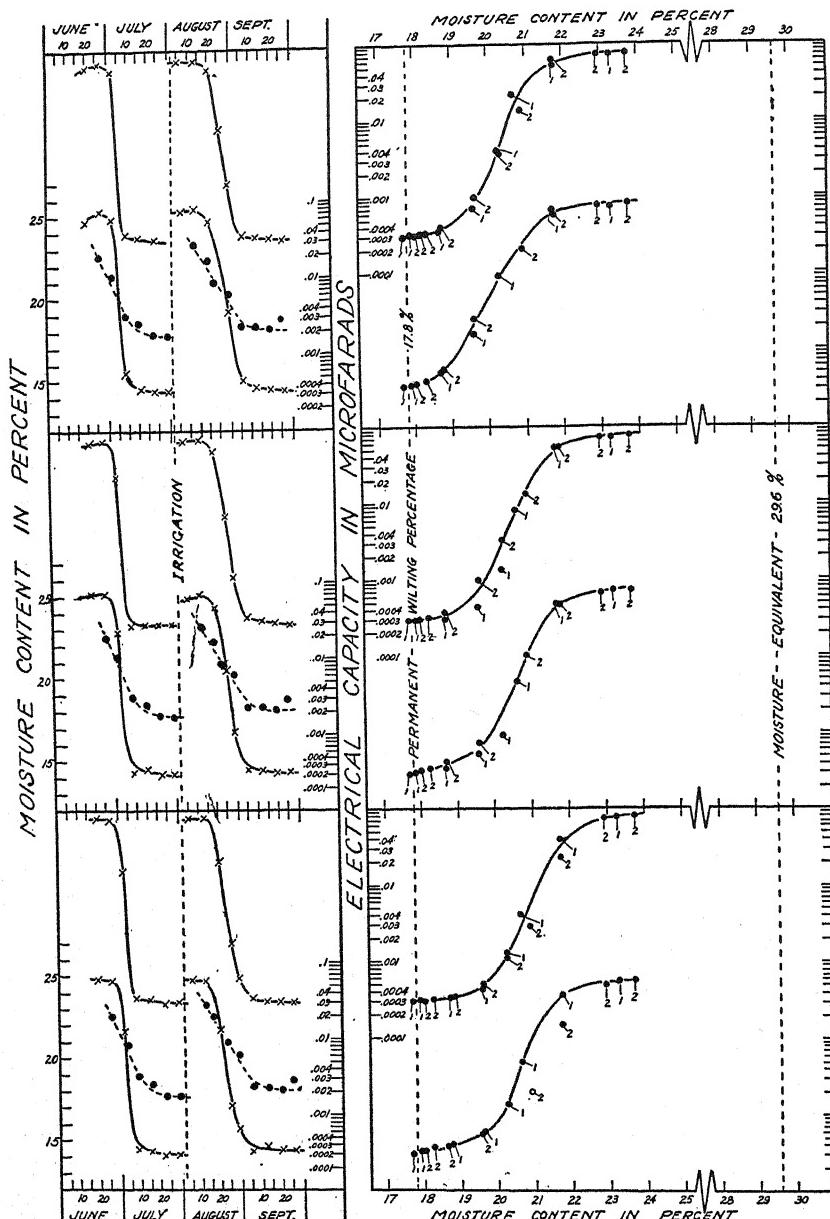
FIG. 3. DEPENDENCE OF ELECTRICAL CAPACITY AND RESISTANCE OF PLASTER OF PARIS
BLOCKS ON MOISTURE CONTENT OF YOLO CLAY IN SUGAR BEET FIELD

Curves on left, for six blocks in groups of two, show the moisture content
(represented by circles) and electrical capacity (represented by crosses) throughout season
for two complete cycles of wetting and drying of the soil. Curves on right are derived from
those on left by plotting simultaneous values of resistance and moisture content. Stag-
gered capacity-scales in center indicate a vertical displacement of origins of adjacent
curves. Number attached to each point indicates the number of cycle from which point
was obtained.
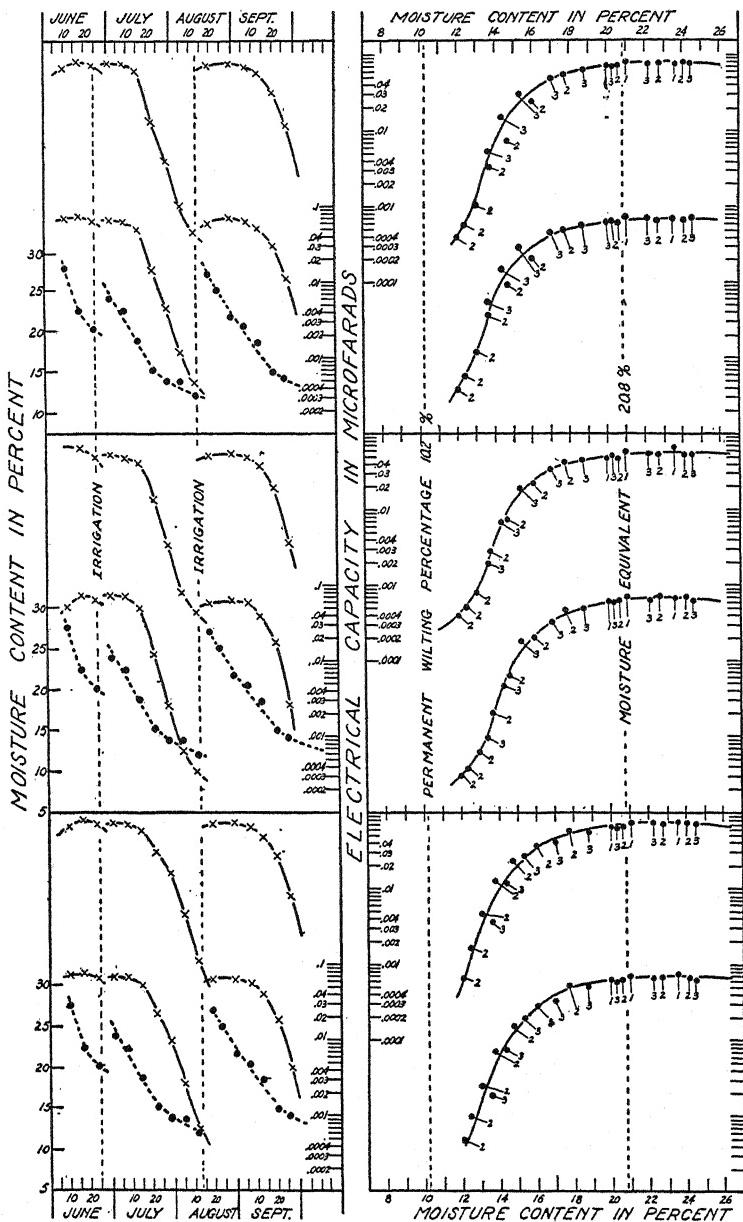
Fig. 4. Dependence of Electrical Capacity and Resistance of Plaster of Paris Blocks on Moisture Content of Yolo Fine Sandy Loam of Sudan Grass Plot

Curves on left, for six blocks in groups of two, show the moisture content (represented by circles) and electrical capacity (represented by crosses) throughout season for three partial cycles of wetting and drying of the soil. Curves on right are derived from those on left by plotting simultaneous values of resistance and moisture content. Staggered capacity-scales in center indicate vertical displacement of origins of adjacent curves. Number attached to each point indicates the number of cycle from which point was obtained.
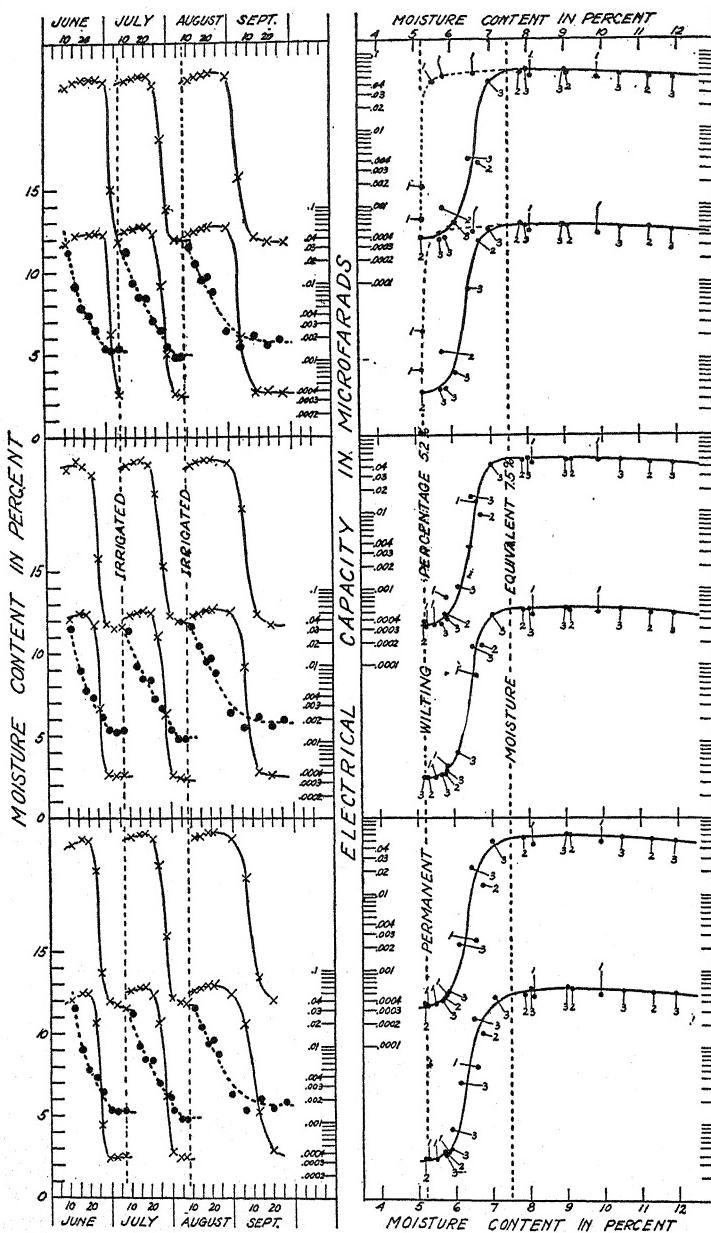
FIG. 5. DEPENDENCE OF ELECTRICAL CAPACITY AND RESISTANCE OF PLASTER OF PARIS
BLOCKS ON MOISTURE CONTENT OF YOLO SAND IN SUGAR BEET FIELD

Curves on left, for six blocks in groups of two, show the moisture content (represented by circles) and electrical capacity (represented by crosses) throughout season for three complete cycles of wetting and drying of soil. Curves on right are derived from the left hand by plotting simultaneous values of resistance and moisture content. Staggered capacity-scales in center indicate vertical displacement of origins of adjacent curves. Number attached to each point indicates the number of cycle from which point was obtained.

very high while the *average* soil-moisture content continually decreases in the main body of the soil.

The limiting minimum observed value of the capacity of the blocks for dry soils is determined both by the capacity of the block alone and (to a slight extent) by the capacity of the leads. The longer and the closer together the pair of leads is, the higher (to a slight extent) is the minimum capacity of the blocks observed at the permanent wilting percentage. This may account for the slightly lower values of the capacities in figure 2 (where the leads were at most 3 feet long) than in figures 3, 4, and 5 (where the leads were more than 50 feet long).

It has been found that there is a slight linear dependence of the dielectric constant of water on the concentration of dissolved salt (5) which continues up to a concentration somewhat below the solubility of plaster of paris. For greater concentrations than this, the dielectric constant has been reported to be independent of salt concentration (4). These observations were made at frequencies around 4 megacycles. If they apply at 1000 cycles, the frequency used here, the electrical capacity of the plaster of paris blocks would seem to be independent of the concentration of dissolved material in the soil solution. This follows because the solubility of the plaster of paris places the concentration of the water of the block in that part of the range where the electrical capacity of the block is independent of the amount of dissolved salt.

When the behavior of the dependence of the electrical capacity is compared with the dependence of the electrical resistance (1) of these blocks on soil-moisture content, it is observed that at about the moisture equivalent of the soil, the electrical capacity is high, the resistance low. As the moisture content decreases, the capacity decreases and the resistance increases rapidly until very close to the permanent wilting percentage of the soil. Here the electrical capacity reaches a seemingly constant value, whereas the resistance continues to increase asymptotically to very high values.

SUMMARY

Laboratory and field investigations have been carried out on the use of the electrical capacity of the 2-electrode plaster of paris block as an indicator of soil-moisture content. The procedure in determining the electrical capacity is similar to that of determining the electrical resistance of the plaster of paris blocks. In both cases the Wheatstone bridge must be balanced with respect to both capacity and resistance. In the first case, though, only the value of the capacity need be noted; in the second case, only the value of the resistance.

The electrical capacity of a plaster of paris block with its electrodes 2 cm. apart is not changed appreciably by variation of as much as 3 mm. in the separation of the two electrodes in the midplane of the block. Also, in comparison to the electrical resistance, the electrical capacity of the plaster of paris blocks should be relatively unaffected by changes in the concentration of the soil solution.

With decrease of soil-moisture content, the electrical capacity of the blocks

begins to drop from a rather high value (approximately 0.070 microfarad) at about the moisture equivalent, finally approaching a relatively constant value (around 0.0003 microfarad) a little above the permanent wilting percentage of the soil.

The dependence of the electrical capacity of the blocks on the soil-moisture content shows, according to our results, an excellent reproducibility and an absence of lag in response of the blocks to changes of soil-moisture content. Our results indicate that the electrical capacity of the plaster of paris block, over the entire range of moisture content readily available to plants, will serve as a practical indicator of the soil-moisture content in a body of soil where the blocks can be buried and where the changes in soil-moisture content are caused by the removal of the moisture by the roots of actively transpiring plants.

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OCCURRENCE OF SOLUBLE SELENIUM IN SOILS AND ITS AVAILABILITY TO PLANTS[1]

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In greenhouse studies it has been found that either the water-soluble or the base-soluble selenium content of a soil is a relatively accurate measure of the amount of "available" selenium in the soil (9). In field studies, however, no correlation between the amounts of these forms of selenium in the surface soil and the selenium content of plants growing on the soil could be found (11). Plant analyses, therefore, have been used in determining the relative "available" selenium content of soils (12). This plant analysis method appears to be the most practicable approach to the problem. The work discussed here was done not with a view toward finding new methods of locating soils of high "available" selenium content, but rather to find an explanation for the discrepancies between greenhouse and field studies. The results of the study reported herein would appear, however, to be of great significance in soil and fertilizer studies in areas of heavy soils and low rainfall.

MATERIALS AND METHODS

The plant and soil collections for these studies were made on a part of the seleniferous land used in earlier work (12). On July 12, 1941, western wheat grass (*Agropyron smithii* Rydb.) was sampled at random over circles 10 yards in diameter at staked locations as shown in figure 1. The samples were dried at 50–60°C. for 48 hours, finely ground in a Wiley mill, and analyzed for selenium by the method described by Moxon (6). Soil samples were taken with a sampling tube at the center of each location. They were air-dried and finely ground with an iron mortar and pestle, and 10-gm. quantities were analyzed for selenium by a modification of the method of Klein (4).

The water-soluble selenium content of the soils was determined by boiling a mixture of 100 gm. of soil and 500 cc. of water for 30 minutes under a reflux condenser. After cooling, most of the solution was filtered off with suction through a thick pad of shredded filter paper, and a 400-cc. aliquot of the clear filtrate was evaporated on the steam bath and analyzed for selenium by the method of Klein (4).

RESULTS AND DISCUSSION

The locations of the samples are shown in figure 1, and the results of the analysis of the plants and of the soils for total selenium are given in table 1.

The data in table 1 show no correlation between the total selenium content of the surface soils and that of the vegetation. This is in agreement with the

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[1] Submitted for publication with the approval of the director of the South Dakota Agricultural Experiment Station as Journal Series Number 158.

work of Byers (2) and of Beath *et al.* (1). A relatively close correlation, however, does exist between the selenium content of the vegetation and that of the second and third feet of soil. At least, plants of high selenium content are not found growing where the selenium content of the soil is low throughout the profile. It appears from the data that parent materials that contain only a few parts per million of the element will only in exceptional cases weather to "toxic" soils unless they are enriched by selenium from other formations. This is in agreement with former work (7).

Perhaps the most important feature of the data in table 1, as concerns these studies, is the relationship between the apparent leaching of selenium in the soils and the selenium content of the plants. With few exceptions, where plants of the higher selenium contents are found the amount of the element in the soil increases with depth. This same observation was made in earlier work (11).
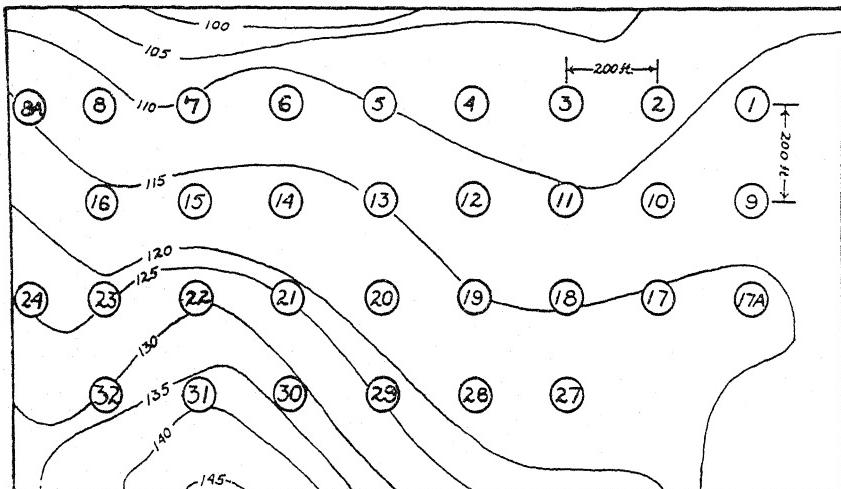
FIG. 1. CONTOUR MAP OF STUDY AREA SHOWING SAMPLING LOCATIONS

This area was in Sec. 2, T. 107N., R. 78 W., South Dakota. [For location on section see (12, fig. 1).]

Beath *et al.* (1) have reported concentrations of soluble selenium in subsoils. These they have attributed indirectly to the presence of "converter" plants. The importance of "converter" plants in the soils studied here is not known, but it appears quite probable that weathering has played the dominant role in the freeing of selenium from its insoluble forms.

The data in table 1 also offer an explanation for the "inaccuracy" of methods used for determining the "available" selenium content of soils in the field, since they indicate that the surface soil may contribute only a small part of the selenium which plants absorb. The question arises, however, as to how much of the selenium leached from surface soils remains soluble at lower levels, since selenite selenium is known to be bound by iron colloids (8, 10, 13) and to be "fixed" in soils (3, 5, 7). It was decided, therefore, to study the soluble selenium content of some of the soils.

Six locations were selected for the soluble-selenium studies. These included soils of high and medium total, high and medium "available," and low "available" but relatively high total selenium content. In order to obtain enough material for the analyses, the soils were resampled at the locations selected. The results of the study are given in table 2.

TABLE 1

Selenium content of soils and related vegetation

Total selenium in p.p.m.

LOCATION*	NO. 8A	NO. 8	NO. 7	NO. 6	NO. 5	NO. 4	NO. 3	NO. 2	NO. 1
Se in *A. smithii*	6	8	79	18	6	5	3	2	2
Se in soils 1st foot	3.7	3.0	4.3	2.7	0.5	2.3	2.6	1.0	0.2
2nd foot	3.5	4.5	15.8	5.5	2.7	2.0	1.3	1.0	2.0
3rd foot	5.6	11.5	29.0	11.5	4.4	0.8	4.4	1.8	4.0

LOCATION		NO. 16	NO. 15	NO. 14	NO. 13	NO. 12	NO. 11	NO. 10	NO. 9
Se in *A. smithii*		22	11	35	6	8	3	1	4
Se in soils 1st foot		4.8	4.2	4.4	2.0	1.6	<0.3	1.7	1.4
2nd foot		8.4	4.1	28.4	3.1	3.2	0.9	1.5	2.6
3rd foot		23.2	4.7	38.4	9.9	6.4	4.5	3.4	2.3

LOCATION	NO. 24	NO. 23	NO. 22	NO. 21	NO. 20	NO. 19	NO. 18	NO. 17	NO. 17A
Se in *A. smithii*	2	14	2	2	7	7	6	4	4
Se in soils 1st foot	3.6	2.7	4.2	4.4	3.7	1.9	1.5	1.3	0.4
2nd foot	5.1	5.4	6.1	4.8	4.1	3.9	2.7	1.3	0.5
3rd foot	5.2	3.7	7.2	6.4	3.8	6.6	3.6	2.2	2.9

LOCATION		NO. 32	NO. 31	NO. 30	NO. 29	NO. 28	NO. 27		
Se in *A. smithii*		2	7	8	12	10	5		
Se in soils 1st foot		5.9	4.6	3.4	4.8	3.9	2.0		
2nd foot		4.6	4.4	4.4	2.9	4.3	4.1		
3rd foot		6.0	4.8	6.0	3.3	4.1	5.3		

* Location numbers correspond to those in figure 1.

The data in table 2 indicate the importance of soluble selenium in soils. Further, they indicate that, as has already been suggested, the second foot and possibly the third foot of soil may be the important source of selenium to plants, thereby explaining the inconsistencies between field and greenhouse studies. Further indications of the importance of the second and third foot of soil in this respect are found in the data in table 3. Large samples of soil from location 7 were obtained at 0–6, 6–12, 12–24, and 24–36 inches. Two clay pots of each of these soils were planted to wheat. The soils were fertilized with equal

amounts of KNO_3 and K_2HPO_4 to increase the growth of the plants. The plants were cut when they were about 8 inches tall and analyzed for selenium. The results are given in table 3.

TABLE 2

Relation of soluble selenium in soils to selenium in vegetation

SOIL LOCATION NUMBER	TOTAL Se CONTENT OF SOILS		SOLUBLE Se CONTENT OF SOILS		Se CONTENT OF A. SMITHII
	p.p.m.		*p.p.m.*		*p.p.m.*
6	1st foot	2.7	1st foot	0.12	18
	2nd foot	5.5	2nd foot	2.76	
	3rd foot	11.5	3rd foot	0.58	
7	1st foot	4.3	1st foot	0.43	79
	2nd foot	15.8	2nd foot	5.00	
	3rd foot	29.0	3rd foot	10.85	
8	1st foot	3.0	1st foot	1.43	8
	2nd foot	4.5	2nd foot	0.48	
	3rd foot	11.5	3rd foot	2.66	
14	1st foot	4.4	1st foot	0.91	35
	2nd foot	28.4	2nd foot	17.60	
	3rd foot	38.4	3rd foot	18.99	
21	1st foot	4.4	1st foot	0.08	2
	2nd foot	4.8	2nd foot	0.10	
	3rd foot	6.4	3rd foot	0.12	
32	1st foot	5.9	1st foot	0.11	2
	2nd foot	4.6	2nd foot	0.05	
	3rd foot	6.0	3rd foot	0.11	

TABLE 3

Selenium content of wheat grown on soils taken at various depths*

DEPTH OF SAMPLE	Se CONTENT OF WHEAT—FRESH BASIS
inches	*p.p.m.*
0–6	4.4
0–6	5.3
6–12	2.9
6–12	3.9
12–24	19.7
12–24	21.2
24–36	14.9
24–36	16.7

* For selenium content of soil see table 2, location 7.

Separate studies on the 24–36-inch sample at location 7 were undertaken to determine the chemical form of the selenium present in these soils. A 100-gm. sample of the soil was extracted twice with water as described before and the

extract was evaporated to about 75 cc. on the steam bath. The concentrated filtrate was filtered into a 100-cc. volumetric flask and made up to volume with water. Two 15-cc. aliquots were analyzed for selenium by the method of Klein (4). Two other 15-cc. aliquots were treated with 25 cc. of 40 per cent HBr and then with sulfur dioxide and hydroxylamine hydrochloride and heated on the steam bath for 30 minutes. The selenium which precipitated was determined by titration (4). Fifteen cubic centimeters of the solution was found to contain 0.162 mgm. of total selenium and 0.153 mgm. of selenium precipitable by sulfur dioxide and hydroxylamine hydrochloride. This indicated that about 95 per cent of the soluble selenium was inorganic. A cold-water extract of 250 gm. of the same soil was made in 500 cc. of water. After being shaken at intervals for a few hours and allowed to stand overnight, the mixture was filtered until about 200 cc. of clear filtrate was obtained. Some 25-cc. portions of this filtrate, treated with 25 cc. of HBr (40 per cent), were saturated with SO_2 and heated on the steam bath for 30 minutes. Other 25-cc. aliquots of the filtrate were made up to $6 N$ H_2SO_4 concentration with $12 N$ H_2SO_4 and saturated with SO_2 and heated on the steam bath for 30 minutes. The solution in H_2SO_4 gave a test so weak that, even upon filtering through asbestos, only a faint pink color was discernible on the mat. Apparently the soluble selenium in this soil was present almost entirely as the selenate, but some selenite selenium appears also to be soluble, since selenites, but not selenates, are precipitated by SO_2 in $6 N$ H_2SO_4 (13).

A 100-gm. sample was extracted twice with boiling water, and the residue from the extraction was dried at 60°C. for 48 hours and then finely ground with an iron mortar and pestle. One half of the residue was then extracted by boiling for 30 minutes with 500 cc. of water. The other half was extracted by boiling with 500 cc. of 1 per cent sodium arsenite solution for 30 minutes. The water was found to remove 0.163 mgm. of selenium; and the arsenite solution, 0.276 mgm. This indicates that selenite is "fixed" in soils, to some extent at least, in the same manner that it is fixed by iron hydroxide in colloidol suspension (10).

To study further the form of selenium in these soils and to compare it with the form occurring in raw shale, a 20-gm. sample of soil containing 29 p.p.m. of selenium from the third foot at location 7 and a 20-gm. sample of finely ground Niobrara chalk containing 30 p.p.m. of selenium were treated as follows. Each sample was boiled for 30 minutes with 200 cc. of water and then cooled and filtered, and the residues were treated twice in the same manner. The filtrates were evaporated to about 50 cc. on the steam bath. The residues were boiled for 5 minutes with 250 cc. of 5 per cent K_2HPO_4 solution and then cooled and filtered. Two subsequent extractions of the residue were made with boiling water to which was added a few grams of $MgCO_3$ to aid in flocculation of the colloids. The combined filtrates from these three extractions were evaporated to 75 cc. on the steam bath. Finally, the residues were boiled twice with 500 cc. of $1 N$ H_2SO_4 for 5 minutes each time, and the filtrate was collected and evaporated to 35 cc., after the addition of 10 cc. of a solution of 5 gm. HgO in 100 cc. of concentrated HNO_3. The residues and the concentrated extracts were then analyzed for selenium. The results are given in table 4.

The data in table 4 indicate that in unweathered rock about half of the selenium is present in a very insoluble form. In the soil studied, therefore, only a few parts per million of the selenium present represents that originally present in the rock, unless weathering of this third foot of soil has caused an oxidation of the selenium to a soluble form. Soil at location 1 is very similar in appearance to soil at location 7 and occurs at about the same contour level, yet it contains only a few parts per million of selenium. These facts, with the occurrence of a stratum of material of fairly high selenium content above location 7, indicate that the selenium in the soils around location 7 is probably largely a deposit from run-off waters from higher elevations. Thus it is possible for seleniferous soils to develop from rock of low selenium content by enrichment from other source material.

TABLE 4

Extraction of selenium from soil and from chalk

SAMPLE	FRACTION	Se IN FRACTION	
		mgm.	*ppm.*
Niobrara chalk	Water	0.066	3.3
	5% K_2HPO_4	0.144	7.2
	$1N$ H_2SO_4	0.136	6.8
	Residue	0.229	11.45
Total......		0.575	28.75
Soil, 24–36 inches	Water	0.401	20.05
	5% K_2HPO_4	0.059	2.95
	$1N$ H_2SO_4	0.123	6.15
	Residue	0.015	0.75
Total......		0.598	29.90

In view of the results obtained for selenium in these soils, it was felt that other elements might also accumulate in subsoils to an extent that surface soil investigations of these elements might lead to erroneous conclusions concerning the fertility of the soils in this region. Investigations already under way have indicated that accumulations of other elements do occur in subsurface soils. It appears, therefore, that soil studies that are confined to surface soils in arid or semi-arid regions may well lead to erroneous conclusions, since the data for selenium indicate the importance of the subsoil in supplying plant nutrients in these areas.

CONCLUSIONS

During the weathering of seleniferous rock to soil in the region in which these studies were made, a large part of the selenium is oxidized to the selenate form. As the selenate, it is leached from the surface to subsurface soils or removed by run-off waters and redeposited at lower elevations, where it may finally leach from the surface and be deposited in subsurface soil.

Though the surface soils of this area may be the source of "available" selenium to plants in many cases, it appears that oftener the subsurface soil is the more im-

portant source. Therefore, selenium studies, in this and similar areas, which are made on surface soils only, probably will lead to erroneous conclusions. It is possible also that this is true for other elements.

The apparent removal and redeposition of soluble selenium by run-off waters accounts in part at least for the difficulties in former work of correlating seleniferous soils with contours in detailed mapping work.

Large variations in the selenium content of plants may occur over relatively short distances on soils that apparently are derived from the same parent material. Every precaution must be exercised, therefore, in making generalizations from the analysis of single-plant collections made over relatively small areas.

SUMMARY

Soils and plants from 32 locations within a small seleniferous area were analyzed for total selenium. Some of the soils were analyzed also for soluble selenium. The results indicate that in the region in which the study was made the second and possibly the third foot of soil are the important source of "available" selenium to plants, and that the top foot of soil is in general relatively unimportant.

Most of the soluble selenium was found to occur as the selenate, but selenite selenium appears also to be present in the soils.

Results obtained indicate that highly seleniferous soils may be formed by the removal of soluble selenium from seleniferous rock and its redeposition in materials of relatively low selenium content.

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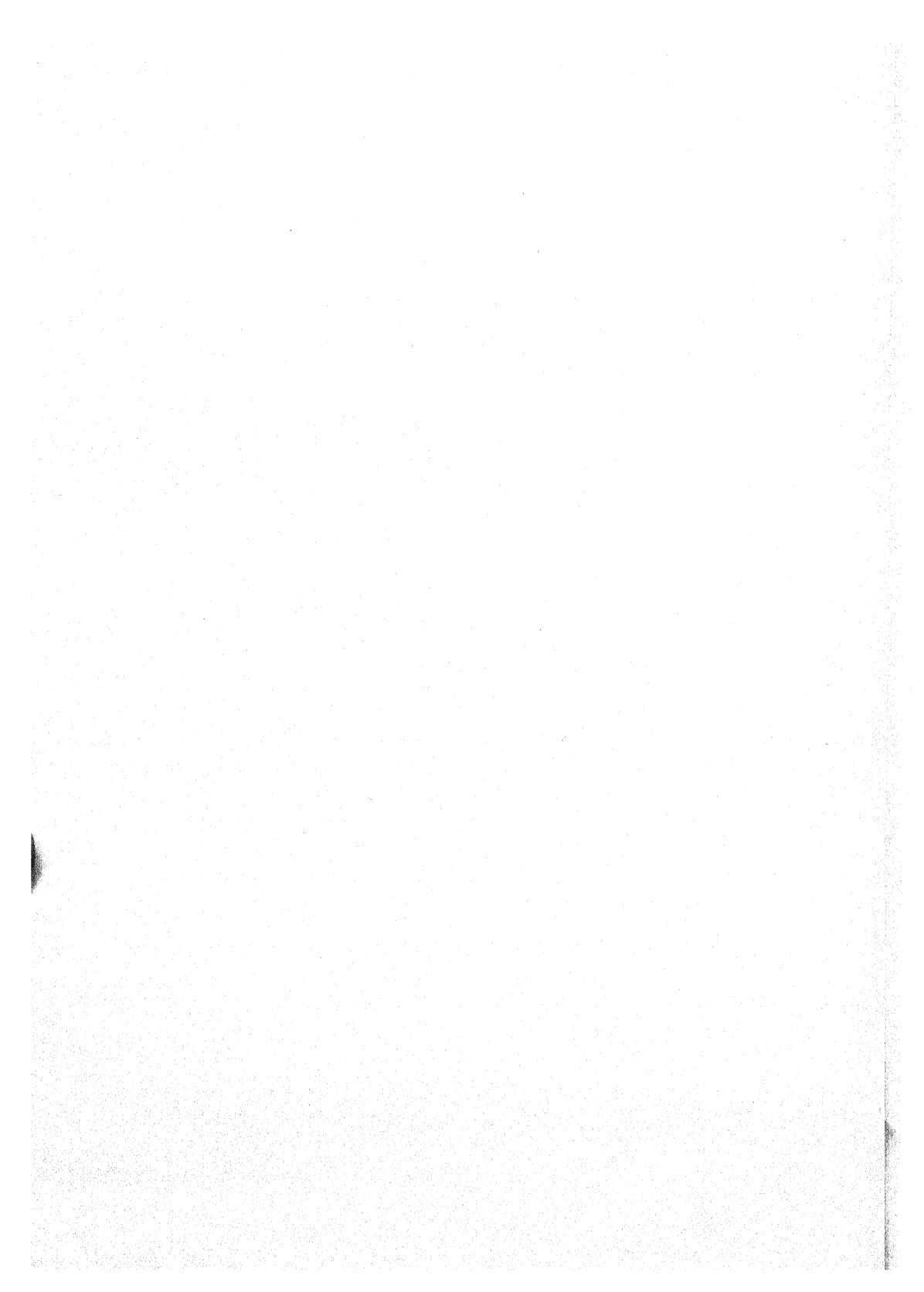
PLANT SYMPTOMS OF BORON DEFICIENCY AND THE EFFECTS OF BORAX ON THE YIELD AND CHEMICAL COMPOSITION OF SEVERAL CROPS[1]

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Plant symptoms have long been used to indicate the deficiency or excess of certain nutrient elements within the soil. Though it is impossible to distinguish all plant needs by certain characteristic symptoms of starvation or toxicity, the values of such symptoms as aids in solving plant nutrition problems is unquestioned. This is especially true in regard to the minor elements, since they compose such a small fraction of the soil and since the quantity necessary for normal plant growth is extremely small. Furthermore, chemical analysis may fail to differentiate between the available and nonavailable forms of the minor elements and for that reason may not always give an accurate indication of the response that plants may make to an application of the elements under consideration. A study of plant symptoms followed by soil and plant analysis should give the most accurate insight into the individual requirements of soils for proper plant growth.

In order to determine what characteristic symptoms are correlated with boron starvation and to obtain plant material for analysis, a number of plants were grown in the greenhouse on boron-deficient soils, with and without borax applied in the culture solution. These were also supplemented in a few cases, with plants from field plats. Plants which showed definite boron-starvation symptoms were analyzed and the results compared with those obtained from the analyses of normal plants. These analyses were made in order to determine whether a correlation exists between the quantity of certain elements in the plant and the symptoms of boron starvation.

HISTORICAL

Numerous investigators (4, 5, 8) have reported increased yields of sugar beets, mangels, turnips, and rutabagas as a result of applications of borax on soils deficient in available boron. Similarly, improved quality of canning beets, cabbage, cauliflower, and celery has been reported (3, 6, 7, 9, 10, 11, 15, 16) to result from applications of this material. Cook (2) described the boron-deficiency symptoms of sugar beets and reported increased yields from applica-

tions of borax and higher percentages of sugar in normal beets than in those suffering from heart rot (boron deficiency).

Caulson and Raymond (4) described turnips suffering from a lack of boron as having a roughened skin on the roots and yellow, mottled, and distorted leaves. Davis and Ferguson (5) reported a darkened, water-soaked condition of the root tissue and hollow centers of turnips deficient in boron.

Boron-deficient radishes, according to Wolf (17), sometimes develop leaves with checked petioles, and Truninger (13) found that radishes grown on pot cultures without borax had characteristic woody cankers on the sides of the roots.

Van Overbeek (14) found that corn leaves were streaked when the plant was grown on a boron-deficient soil.

Various explanations have been advanced for the physiological breakdown of the tissue of many plants suffering from boron starvation. Schmidt (12) has expressed the opinion, based on experimental data, that plants suffering because of insufficient boron absorb more nitrate nitrogen than is needed and that the cells break down as a result of the high nitrate concentration. It has also been suggested that boron functions as a regulator of the permeability of the plasma membrane and hence influences the intake of certain ions.

MATERIALS AND METHODS

The greenhouse experimental procedure may be summarized as follows: Crops were grown in 1-gallon glazed earthenware jars filled with soil or quartz sand. Adequate quantities of all nutrient elements with the exception of boron were supplied, as shown in table 1. Uniform moisture relationships were maintained in all jars by frequent weighing and additions of distilled water.

All crops, except dandelions were grown from seed, and the number of plants per jars was kept uniform for each individual crop by early thinning or by transplanting. Dandelions were transplanted from a lawn to the pot cultures. Yields of this crop were not recorded. Wheat, of a winter variety, was planted in the fall and left out of doors until midwinter.

Sugar beets, canning beets, corn, turnips, dandelions, barley, and wheat were grown in jars containing Thomas sandy loam. Mangels, radishes, and chicory were grown in quartz sand cultures.

Borax was applied to the crops at the following rates per area: sugar beets, 10 and 20 pounds; canning beets, 10 pounds; corn, 5 and 10 pounds; turnips and dandelions, 5 pounds; and barley and wheat, 2.5 and 5 pounds. Mangels, radishes, and chicory were treated at single rates of 2.5, 5.0, and 3.5 pounds, respectively.

To supplement the analyses made on plants grown in greenhouses cultures, field samples of three different crops were taken. Sugar beet samples were obtained from a field of Thomas sandy loam and were divided according to the appearance or nonappearance of boron-deficiency symptoms. The same procedure was followed with rutabagas grown on Brookston clay loam.

Samples of canning beets were taken from plats in a field experiment con-

ducted on Emmet sandy loam. The samples were selected at random from eight plats on two different farms. Borax had been broadcast at the rate of 40 pounds per acre on four of the plats, and the other four had received no borax. The percentages of beets in the random samples showing internal black spots (boron deficiency) were determined by slicing the beets.

Standard laboratory methods were used in the chemical analyses of plant tissue. Insufficient material in many cases limited the number of chemical determinations that could be made. All analyses were made on plant tissue dried in the oven at 65°C.

Boron was determined by the Berger-Truog method (1). Calcium and magnesium were determined on the same ash samples, calcium by titrating the oxalate with standardized potassium permanganate, and magnesium by the gravimetric pyrophosphate method. The percentage of iron was found in the tissue by titrating the ferric ion with dilute standardized titanium trichloride. The Gunning modification of the Kjeldahl method was used to determine nitrogen. Potassium was determined by the chloroplatinate method.

TABLE 1

Nutrient elements applied to greenhouse pot cultures

NUTRIENT	QUANTITY PER POT	ACRE-EQUIVALENT QUANTITY	NUTRIENT	QUANTITY PER POT	ACRE-EQUIVALENT QUANTITY
	gm.	lbs.		gm.	lbs.
$FePO_4$*	1.000	500.0	$MnSO_4 \cdot 4H_2O$	0.008	4.0
$CaHPO_4 \cdot 2H_2O$*	0.500	250.0	NaI	0.001	0.5
KNO_3	0.500	250.0	$Al_2(SO_4)_3 \cdot H_2O$	0.013	6.3
$Ca(NO_3)_2 \cdot 4H_2O$	0.250	125.0	$ZnSO_4$	0.005	2.5
$MgSO_4 \cdot 7H_2O$	0.250	125.0	$CuSO_4$	0.005	2.5
$NaCl$	0.005	2.5	$Ca(H_2PO_4)_2$†	0.144	72.0

* Applied separately as dry salt to sand cultures.

† Applied separately in solution to Thomas sandy loam pot cultures.

EXPERIMENTAL RESULTS

Sugar beets

The death of the growing center of the sugar beet crown, as a result of boron deficiency, has been designated as "heart rot." The first signs of boron starvation occurred in the leaves in the form of blackened and checked petioles, some of them being twisted and shortened. On some of the plants the leaves were smaller and more numerous than on normal plants.

Many of the beets grown with an insufficient supply of boron showed signs of breakdown in the root tissue. This appeared as a discoloration of the flesh and as external cankers resulting from complete disintegration and sloughing off of a part of the root.

Only a few of the beets grown in this experiment actually developed dead or rotten hearts. This indicates that the other symptoms of boron starvation are more common than the actual death of the heart tissue.

Borax applied in pot cultures at the rate of 10 pounds per acre prevented heart rot and, as shown in table 2, increased the yield of both roots and tops. The 20-pound application of borax resulted in a slightly greater yield of tops but a smaller yield of roots than the 10-pound treatment.

The fact that boron starvation markedly affects the composition of sugar beet plants is also shown by the results in table 2. The boron content of the dried tops and roots was increased by the borax applications to pot cultures. Field-grown beets having heart rot contained exactly the same quantity of boron as did similarly affected beets grown in pot cultures, and normal field-grown beets contained but 1 p.p.m. more than did those grown in pot cultures treated with 20 pounds of borax per acre.

In contrast to the increase in the boron content of both roots and tops of beets grown in the greenhouse with applications of borax, the content of iron found

TABLE 2

Effect of borax and apparent boron starvation on yield and mineral analysis of sugar beets grown on Thomas sandy loam

BORON SUPPLY*	YIELD PER POT		BORON		Fe₂O₃		N		K₂O	MgO		CaO	
	Roots	Tops	Roots	Tops	Roots	Tops	Roots	Tops	Roots	Roots	Tops	Roots	Tops
	gm.	*gm.*	*p.p.m.*	*p.p.m.*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Pot cultures† { No borax	46.7	109.0	10	10	0.023	0.129	0.90	2.29	0.90	0.90	1.95	0.47	1.80
10 lbs. borax	90.4	131.4	14	20	0.013	0.098	0.76	1.63	0.91	0.76	1.74	0.44	1.60
20 lbs. borax	81.7	136.6	15	24	0.014	0.106	0.75	1.62	0.91	0.75	1.75	0.42	1.80
Field samples { Boron-deficient	....	.....	10		0.028		2.16		1.21	0.96		0.34	
Normal	....	.....	16		0.011		1.54		1.33	0.68		0.23	

* The pot cultures received borax at rates equivalent to 0, 10, and 20 pounds per acre.
† Average of six replications.

in the same fractions decreased. It was also found that field-grown beets having heart rot were much higher in iron than were normal beets. Apparently an inverse relationship exists between the boron and iron contents of the crop.

An inverse relationship was found to exist also between boron and nitrogen. Beets with heart rot, low in boron, were high in nitrogen. Borax applications not only eliminated the heart rot and raised the boron content but greatly reduced the nitrogen content of sugar beets. A similar relationship was found in the field samples; the beets with heart rot contained considerably more nitrogen than did normal beets from the same field.

Field-grown sugar beets with heart rot were lower in potassium content than were normal beets. These results vary from those obtained with greenhouse cultures, in which there was no apparent change in the potassium content as a result of the application of borax.

The 10-pound application of borax per acre produced only slight changes in

the calcium and magnesium contents of the sugar beet plants grown in pot cultures. The data indicate, however, a general trend toward higher percentages of these elements in plants grown in a medium containing an insufficient supply of boron. This trend was evident also in the samples obtained from the field.

Canning beets

Much similarity was found between the symptoms of boron deficiency in canning beets and in sugar beets. Leaf symptoms were less common than for sugar beets but may be similarly described. One difference was noticed. Leaves of canning beets, naturally of a reddish green color, became more intensely red when starved for boron.

Root symptoms of boron deficiency occurred as dark-colored areas of corky tissue in some instances in the central parts, but more commonly near the surface; in fact, in some of the roots the corky areas were so close to the surface

TABLE 3

Effect of borax on yield, quality, and boron and nitrogen contents of canning beets

	BORAX APPLIED PER ACRE	YIELD PER POT*		BLACK SPOT†	BORON		NITROGEN	
		Roots	Tops		Roots	Tops	Roots	Tops
	lbs.	*gm.*	*gm.*	*per cent*	*p.p.m.*	*p.p.m.*	*per cent*	*per cent*
Pot cultures‡............	0	2.5	7.9	.....		7.5		1.78
	10	7.3	14.9			27.5		1.45
Field samples§...........	0			54.30	17.3		2.01	
	40			5.96	19.9		2.02	

* Average of three replications.
† Average of four replications.
‡ Grown on Thomas sandy loam.
§ Grown on Emmet sandy loam.

that they included the epidermis and thus appeared as external cankers. The roots of boron-deficient plants were flattened and less symmetrical than were those of normal plants.

As shown in table 3, the growth of canning beets in pot cultures was greatly stimulated by the application of borax. Applied broadcast in the field at the rate of 40 pounds per acre, borax did not increase yields but, as shown in table 3, was very effective in reducing the number of roots containing internal black spots.

Analyses of the tops of the beets grown in pot cultures showed that an application of 10 pounds of borax per acre increased their boron content and decreased their nitrogen content. Roots grown in the field on soil treated with borax contained more boron than did beets grown on soil which did not receive borax, but no difference was found in the nitrogen content.

Mangels

Boron-deficiency symptoms of mangels were very similar to those of sugar beets. The checking of the petioles was not so prominent as in sugar beets,
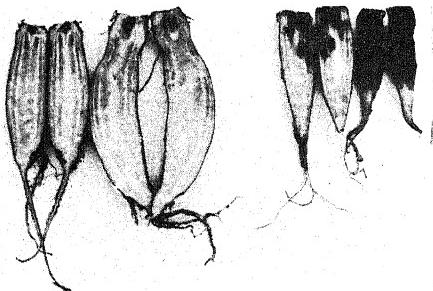
FIG. 1. EFFECT OF BORAX ON GROWTH AND
QUALITY OF MANGEL ROOTS GROWN
IN SAND CULTURES

Left—2.5 pounds of borax per acre;
right—no borax.
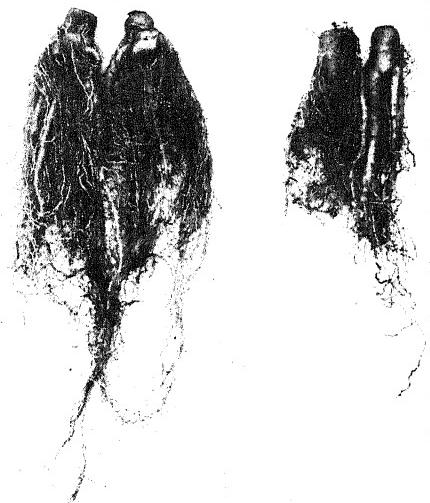
FIG. 2. EFFECT OF BORAX ON GROWTH OF
CHICORY ROOTS IN SAND CULTURES

Left—3.5 pounds of borax per acre; right
—no borax.
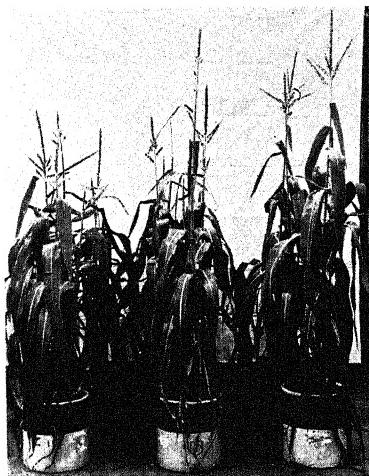
FIG. 4. EFFECT OF BORAX ON GROWTH
OF CORN IN THOMAS SANDY LOAM
POT CULTURES

Left—no borax; center—5 pounds
of borax per acre; right—10 pounds.

FIG. 3. EFFECT OF BORAX ON GROWTH OF BAR-
LEY IN THOMAS SANDY LOAM POT CULTURES

Left—no borax; center—2.5 pounds of borax
per acre; right—5 pounds. Note difference in
heading.

FIG. 5. EFFECT OF BORAX ON BLOSSOMING OF DANDE-
LIONS IN THOMAS SANDY LOAM POT CULTURES

but shortened, twisted, and deformed leaves were found on all the plants in the cultures that did not receive borax. The leaves in the centers of the crowns died, and numerous small leaves came out from the edges of the crowns. The new leaves were generally at right angles to the crown, giving the plant a flattened appearance.

All the roots in the pot cultures showed internal breakdown of the tissue, as illustrated in figure 1. Several of the roots were so seriously affected that the epidermis was broken down to form external cankers like those common with sugar beets.

As shown in table 4, a 2.5-pound-per-acre application of borax almost trebled the yield of roots and doubled the yield of tops. The application also markedly increased the boron content of the plants but reduced the concentrations of nitrogen and iron. With several crops the increase in boron content as a result

TABLE 4

Effect of borax on yield and partial analysis of mangels, radishes, and chicory grown in sand cultures

CROP	BORAX AP-PLIED PER ACRE	YIELD PER POT		BORON		NITROGEN		Fe_2O_3		K_2O
		Roots	Tops	Roots	Tops	Roots	Tops	Roots	Tops	Roots
	lbs.	*gm.*	*gm.*	*p.p.m.*	*p.p.m.*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Mangels*	0	7.8	4.2	7.5	17.5	1.36	1.53	0.014	0.035	
	2.5	22.6	8.7	10.0	50.0	1.02	1.35	0.011	0.029	
Radishes†	0	53.9	31.5	17.5	20.0	2.88	4.25	0.064	0.032	
	5.0	57.7	53.9	20.0	37.0	2.52	4.08	0.043	0.023	
Chicory*	0	24.9	15.6	7.0	14.0	0.34	1.15	0.014	......	1.32
	3.5	32.4	19.6	9.0	28.0	0.22	1.07	0.011	......	1.17

* Average of three replications.
† Average of four replications.

of application of borax was greater in the tops than in the roots. This relationship was very marked with mangels; the increase in the roots was from 7.5 to 10 p.p.m. whereas that in the tops was from 17.5 to 50.0 p.p.m.

Radishes

Except for the size of the tops, radishes did not show symptoms of boron deficiency. The yield of roots was only slightly increased by the 5-pound-per-acre application of borax, but the yield of tops was increased from 31.5 to 53.9 gm. per pot.

As with mangels, the borax application slightly increased the boron content of the roots and greatly increased that of the tops (table 4). Nitrogen and iron contents of both roots and tops were reduced about equally by the borax application.

Chicory

When starved for boron, chicory made only a stunted growth. Many of the leaves were twisted, and the petioles and midribs of the leaves were weakened. As a result of this condition, some of the leaves were broken, and those not broken failed to stand erect as did the leaves of normal plants. A very pronounced reddening occurred in the leaves of boron-starved plants. The normal plant, as indicated in figure 2, had a much larger and more fibrous root system. No internal breakdown of the tissue could be detected in any of the roots.

The application of 3.5 pounds of borax per acre (table 4) markedly increased the yield and boron content of chicory. As in the other root crops, the increase in boron content was much greater in the tops than in the roots. The borax treatment caused a decrease in the nitrogen content of both roots and tops and a decrease in the amounts of iron and potash in the roots.

Rutabagas

The leaf symptoms of boron deficiency in rutabagas were less marked than were those in the sugar beet. Some of the leaves died prematurely, but there were fewer deformed leaves than were found on either sugar beets or mangels.

TABLE 5

Partial analysis of normal and boron-deficient rutabagas grown on Brookston clay loam

SYMPTOMS	BORON		NITROGEN		Fe₂O₃	
	Roots	Tops	Roots	Tops	Roots	Tops
	p.p.m.	*p.p.m.*	*per cent*	*per cent*	*per cent*	*per cent*
Normal......................	15	30	2.15	2.19	0.036	0.228
Boron-deficient...............	10	20	2.23	2.43	0.078	0.499

The most pronounced symptoms were found in the roots. As in most cases of boron deficiency in root crops, there was an internal breakdown of the tissue. Instead of cankers, however, the roots developed "water-core" or "brown-heart," a condition which appeared as dark brown water-soaked areas in the central parts of the roots. These areas varied from small spots to those comprising most of the interior of the roots.

As indicated in table 5, normal rutabagas, both roots and tops, were higher in boron content and lower in nitrogen and iron than the plants which showed symptoms of boron deficiency. The difference in iron was very marked: the plants deficient in boron, as judged both from symptoms and boron content, contained twice as much iron as the normal plants.

Turnips

A few small spots in the roots of turnips grown in the cultures without borax indicated a condition similar to that reported as "brown-heart." That this condition did not become more serious is probably due to the fact that the roots were small. MacLeod (8) has reported that "brown-heart" is not usually found in roots smaller than 2 inches in diameter.

As shown by the data in table 6, an application of 5 pounds of **borax** per acre caused a 20 per cent increase in the yields of turnips.

Barley

The barley plants, except for a slightly heavier growth in the borax-treated pots, showed very little response to boron until the plants started to head. The time of heading, as indicated in figure 3, was advanced about 10 days by the borax application. Some of the plants in the untreated pots failed to produce an appreciable quantity of grain.

The yield of the entire top growth was increased about 43 per cent by the 2.5-pound-per-acre borax application. Only a slight additional increase resulted from the heavier borax application.

TABLE 6

Effect of borax on yields of turnips, barley, and wheat grown in Thomas sandy loam pot cultures

CROP	BORAX APPLIED PER ACRE	YIELD PER POT	
		Roots	Tops
	lbs.	*gm.*	*gm.*
Turnips*....................	0	54.7	44.2
	5.0	66.0	49.2
Barley†....................	0		3.2
	2.5		4.6
	5.0		4.9
Wheat†....................	0		18.8
	2.5		20.8
	5.0		19.3

* Average of two replications.
† Average of three replications.

Wheat

No actual symptoms of boron deficiency were apparent in wheat, although the plants that received borax headed a few days earlier than those that did not receive borax. This earlier heading was an indication that the wheat actually needed the boron, although as shown by the data in table 6 the increase in yield was only slight. The 5-pound-per-acre application was apparently too heavy, as the yield was smaller than that obtained from the 2.5-pound application.

Corn

The corn plants grown in pot cultures deficient in available boron were later in tasseling than were those that received borax. As with chicory, boron-deficient corn leaves were tinged with red, whereas the plants grown in cultures treated with borax had normal green leaves. The leaves were not streaked as reported by Van Overbeek (14).

As shown in table 7 and indicated in figure 4, yields of corn were considerably

increased by the application of borax. From the data it appears that corn needs more borax than does barley or wheat. This is indicated by the larger yields from the pots treated with 10 pounds of borax per acre in comparison with those that received only 5 pounds. The data seemed to indicate that 2.5 pounds was enough for barley and that 5 pounds was too much for wheat. More data are necessary, however, before this relationship can be definitely established.

The corn that received borax had a much higher boron content and a somewhat lower iron content than that which did not receive borax (table 7). These results are similar to those obtained with several other crops. The data concerning nitrogen content are not in accord with those from other crops, however, for the nitrogen content of corn was not affected by the borax.

Dandelions

No definite leaf symptoms of boron deficiency were noticed in the dandelions grown in pot cultures, but the plants treated with borax made a more luxuriant growth and the leaves stood more erect than those that received no treatment.

TABLE 7

Effect of borax on yield and partial analysis of tops of corn grown in Thomas sandy loam pot cultures

BORAX APPLIED PER ACRE	YIELD PER POT*	BORON	NITROGEN	Fe₂O₃
lbs.	*gm.*	*p.p.m.*	*per cent*	*per cent*
0	86.5	5	1.20	.052
5	103.5	15	1.26	.045
10	117.4	18	1.18	.046

* Average of four replications.

It was found, further, that all the plants which received borax blossomed profusely, but not a single blossom was produced on the 12 plants which did not receive borax. Figure 5 presents a comparison of the plants.

SUMMARY AND CONCLUSIONS

A number of crops—sugar beets, canning beets, mangels, radishes, chicory, rutabagas, turnips, barley, wheat, corn, and dandelions—were grown on either a boron-deficient soil or on boron-deficient quartz sand, and on similar substrates to which borax had been added. These crops were grown to determine boron-deficiency symptoms and to provide normal and boron-deficient plant tissue for chemical analysis.

An insufficient supply of boron for root crops was evidenced by the distortion and premature death of the central leaves, by the formation of numerous small leaves, and by a breakdown of the root tissue cells. The formation of corky tissue, sloughed-out areas (cankers), and water-soaked areas (brown-heart) accompanied or followed the breakdown of the root tissue cells. The cereals—barley, wheat, and corn—matured later and failed to develop seeds normally

when boron was lacking. Dandelions with an insufficient supply of boron failed to bloom.

Certain crops were analyzed for boron, calcium, nitrogen, potassium, magnesium, and iron to determine a possible correlation between the mineral content of these crops and the supply of available boron in the soil. The tissue of plants inadequately supplied with boron contained, in most cases, higher percentages of calcium, nitrogen, magnesium, and iron than the tissue of plants grown in the presence of sufficient boron. The greatest differences in composition occurred in the contents of nitrogen and iron. The potassium content was not greatly altered by the plants' response to boron. Borax applied to the soil in all cases increased the boron content of the plants. Plants with characteristic boron-deficiency symptoms were relatively low in boron content.

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FOREST SOIL STUDIES: II. CHANGES IN MICROFLORA AND CHEMICAL COMPOSITION OF DECOMPOSING TREE LEAVES[1]

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The importance of the humus layer in the growth and reproduction of forests is generally recognized. Variations in the character of the humus layer usually have been associated with the rate of decomposition. Thus mull has been represented as forming under conditions favorable to decomposition, whereas mor is found where decomposition is slow. Recent studies by Broadfoot and Pierre (3) have shown that the rate of decomposition is related to the excess base, water-soluble organic matter, and nitrogen content of the leaves. The water-soluble organic matter showed a high correlation with decomposition during the early stages, but this became less important as decomposition progressed. The nitrogen content, likewise, became less important with passage of time. On the other hand, the excess base became more closely related to decomposition in the later periods. Their results indicate that several interrelated specific chemical properties of leaves affect the rate of decomposition. The explanation of mull and mor formation, on the basis of rate of decomposition, however, has not been entirely satisfactory. Romell (10) found that the rate of decomposition in a certain type of mor was more rapid than that in a nearby mull. As a result of this and other observations, he proposed a biological explanation (11) of mull and mor formation in which the formation of various types of humus layers is attributed to differences in the type of decomposition of various constituents rather than to differences in the rate of decomposition.

Regardless of which explanation is accepted, the soil flora is recognized as having an important role in determining the nature of the humus layer. It seemed desirable, therefore, to make some further studies of decomposition with certain selected leaves to determine both the changes in microbial population on different leaves as decomposition progressed, and the changes in the character of the organic matter during decomposition.

MATERIALS AND METHODS

The leaf samples selected were table mountain pine (*Pinus pungens*, Lamb), beech (*Fagus grandiflora*, Ehrh.), red maple (*Acer rubrum*, L.), yellow poplar (*Liriodendron tulipifera*, L.), red oak (*Quercus rubra*, L.), and black walnut (*Juglans nigra*, L.). These represent leaves with a wide range in rates of decomposition and in excess base as determined by Broadfoot and Pierre (3).

[1] Contribution from the departments of plant pathology and bacteriology and agronomy and genetics. Published with the approval of the director of the West Virginia Agricultural Experiment Station as scientific paper No. 282.

Samples of mature leaves, plucked from the tree, or clean leaves freshly fallen, were air-dried and ground in a Wiley mill. One-hundred-gram portions were placed in 2000-ml. Erlenmeyer flasks, moistened, and inoculated with a soil suspension from a mixed forest stand. Additional water was added to bring the moisture content up to the water-holding capacity as determined by the Bouyoucos method (2). The flasks were then plugged with cotton, covered with wax paper to reduce evaporation, and incubated in the dark at 25°C. Additional water was added at each sampling to maintain nearly constant moisture conditions. Samples were removed at 1, 2, 4, 8, 16, and 32 weeks for determination of numbers of organisms and at 8, 16, and 32 weeks for chemical analysis.

Numbers of microorganisms. The leaves were thoroughly mixed, and a sample representing approximately 1 gm. of dry leaves was accurately weighed and transferred to a sterile 100-ml. water blank. After thorough shaking, serial dilutions were made in the usual manner. Duplicate plates using sodium caseinate sugar [medium 4 (7)] for bacteria, and peptone glucose acid agar [medium 18 (7)] for fungi were made and incubated at room temperature for 6 days. The plates having between 50 and 300 colonies were counted with the aid of a Quebec colony counter. The numbers were then calculated to the basis of 1 gm. of oven-dry leaves. Nitrifying bacteria were determined by inoculating ammonium-sulfate and sodium-nitrite media from the various dilutions. Cellulose-decomposing bacteria were determined on cellulose media (7).

pH. The pH was determined by means of a glass electrode, 1 gm. of the sample being used in 10 ml. of distilled water.

Ether extract. The ether-extractable matter was removed by extracting 5 gm. of air-dry sample for 24 hours in a Soxhlet extractor. The ether was evaporated and the residue dried at 105°C. and weighed.

Water-soluble. The ether-extracted leaves were extracted with 100 ml. of water for 24 hours, and the residue was filtered and washed with 150 ml. of distilled water. The residue was then refluxed for 3 hours with 100 ml. of water, filtered, and washed with 150 ml. of hot water. Aliquots from the cold and hot water were evaporated, dried, and weighed. The sum of the two extractions is reported as water-soluble.

Cellulose and lignin. The percentages of cellulose and lignin were determined according to the method of Norman et al. (8, 9). A slight modification was made in the technique as outlined by the original authors. This consisted in centrifuging the suspensions before passing the supernatant liquid through a cloth filter supported by a Gooch crucible. The residue on the filter cloth was returned to the centrifuge tube, and the entire sample was washed before the next treatment. It was found that this method expedited filtration.

The results reported here are the average values obtained from closely agreeing duplicate or triplicate analyses. In each instance the results of the proximate analysis were calculated to the original weight of the leaves used.

RESULTS

Changes in microbial population

Isolations of both fungi and bacteria from the various samples during the course of the experiment showed no consistent differences in types of organisms. Repeated experiments failed to show the presence of nitrifying bacteria in any of the leaves tested. Similarly, the cellulose-decomposing bacteria were found only occasionally and then in small numbers during the latter stages of the decomposition of black walnut and yellow poplar leaves. They could not be demonstrated for the other leaves at any time. The principal bacteria noted were gram-negative rods belonging to the Achromobacter and Flavobacterium genera with a smaller number of members of the *Bacillus subtilis* group. The
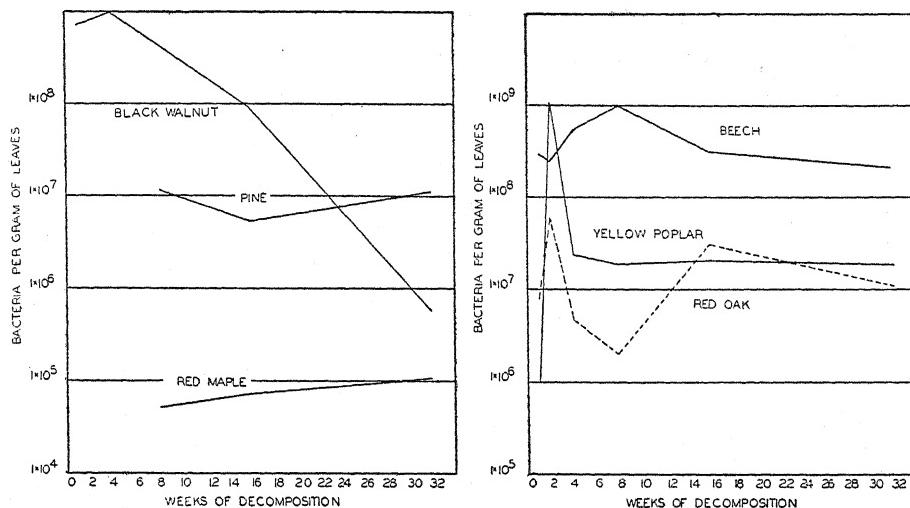
FIG. 1. BACTERIAL POPULATION OF DECOMPOSING LEAVES

fungi consisted of five species of Penicillium; one species each of Oospora, Alternaria, Cephalosporium, Mucor, and Cylindrotricum; and *Aspergillus niger*.

Bacteria. The changes in the bacterial count of the leaf samples are shown in figure 1. The red maple leaves showed the smallest change in the bacterial population of all of the leaves studied. During the first 4 weeks, the plates were covered with fungi and no counts could be made. At 8 weeks the numbers of bacteria increased to a describable value and continued to increase until the end of the 32-week period. Bacterial numbers in the pine sample followed a course somewhat similar to that of the red maple, but were maintained at a higher level. Black walnut leaves showed an enormous increase in bacterial numbers during the first week. This was followed by a further slight increase during the next 3 weeks, after which the number decreased rapidly throughout the remainder of the period of study.

A rapid initial increase in number also took place in the yellow poplar leaves. This was followed by a rapid decrease during the second 2-week period, after which the numbers remained nearly constant. Beech leaves showed an increase during the first 8 weeks, followed by a gradual decline. The population curve of bacteria in the red oak leaves showed two peaks: the first appeared after a rapid increase in numbers during the first 2 weeks of decomposition, and the second occurred at 16 weeks.

Fungi. The changes in numbers of fungi are shown in figure 2. A very rapid growth of molds took place in the red maple leaves during the first 2 weeks of the decomposition period. Numbers continued to increase up to 4 weeks then dropped off rapidly. A second peak was reached at 16 weeks, after which there was little change in numbers. Molds did not increase so rapidly in the pine as
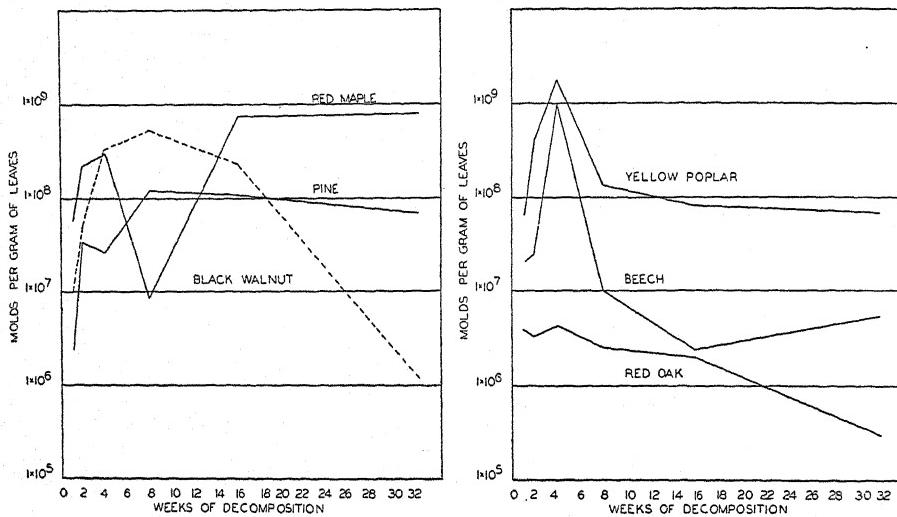
FIG. 2. FUNGUS POPULATION OF DECOMPOSING LEAVES

in the red maple. In general, the numbers increased for the first 8 weeks; a slight decrease occurred for the rest of the period. Black walnut leaves showed a rapid increase in the number of molds during the first 4 weeks. The peak was reached by the end of 8 weeks. The population then decreased rapidly for the rest of the period.

In both yellow poplar and beech leaves there was a rapid increase in numbers during the first week. The peak in population was reached in 4 weeks. This change was followed by a rapid decline in both instances until the eighth week. Thereafter, in the yellow poplar, the decline was only slight until the end, whereas in the beech there was a slight increase from the sixteenth to the thirty-second week. Red oak leaves showed the lowest count of all the material tested. There was a rapid increase during the first week, with little further change until the end of the fourth week, after which a slow decline occurred which continued to the end of the experimental period.

Changes in reaction

As shown in figure 3, the leaves may be divided into three groups on the basis of their changes in reaction during decomposition. The high-acid group is composed of red maple and pine leaves. In both of these the initial pH was slightly below 4. Red maple became more acid during the first week, after which the acidity steadily decreased. The pine became slightly more alkaline in reaction during the first week. This was followed by a slight fall in pH during the next 3 weeks. Thereafter the reaction became steadily less acid until the end of the experiment. In both instances the reactions had increased more than 1 pH unit, but at the conclusion of the experiment they were still distinctly acid.

The four remaining samples had initial reactions between pH 5.0 and 5.5. The changes in reaction during decomposition were sufficiently different, however, to separate beech and red oak from black walnut and yellow poplar.
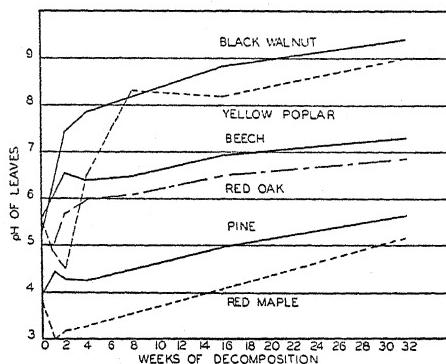
FIG. 3. CHANGES IN pH DURING DECOMPOSITION OF LEAVES

Of the first group, red oak was slow to show a change in reaction. An increase of 1 pH unit occurred between the second and the fourth weeks. This was followed by a gradual increase which continued until the end of the thirty-second week, when the neutral point was nearly reached. The beech leaves did not show the initial lag period. The pH increased nearly 1 pH unit during the first 2 weeks. This was followed by a slight decrease, but, beginning at the fourth week, the course of the reaction changed and continued to go upward until it passed slightly beyond the neutral point.

In the initial stages, the course of the reactions of black walnut and yellow poplar leaves took opposite directions. During the first 2 weeks the pH of yellow poplar dropped nearly 1 pH unit, then it rose rapidly until the eighth week and remained nearly constant until the sixteenth week. By the end of the experiment, the reaction was well in the alkaline range, having increased nearly $3\frac{1}{2}$ units above the original value. The pH of black walnut increased $2\frac{1}{2}$ units during the first 4 weeks. Thereafter, the increase was gradual, until a pH of 9.4 was reached at the conclusion of the period of decomposition.

Changes in chemical composition

The chemical composition of the decomposing leaves is shown in figure 4.

Ether-soluble material occurred in the smallest amounts of any of the constituents tested. The highest content (12 per cent) was found in black walnut; the lowest initial content (3.9 per cent), in yellow poplar. In all cases there was decomposition. The greatest total loss, 10.7 gm. per 100 gm. of leaves, occurred in black walnut; the smallest (0.7 gm.), in red oak. Whenever a pronounced decomposition of ether-soluble material took place, this occurred largely during the first 8-week period.
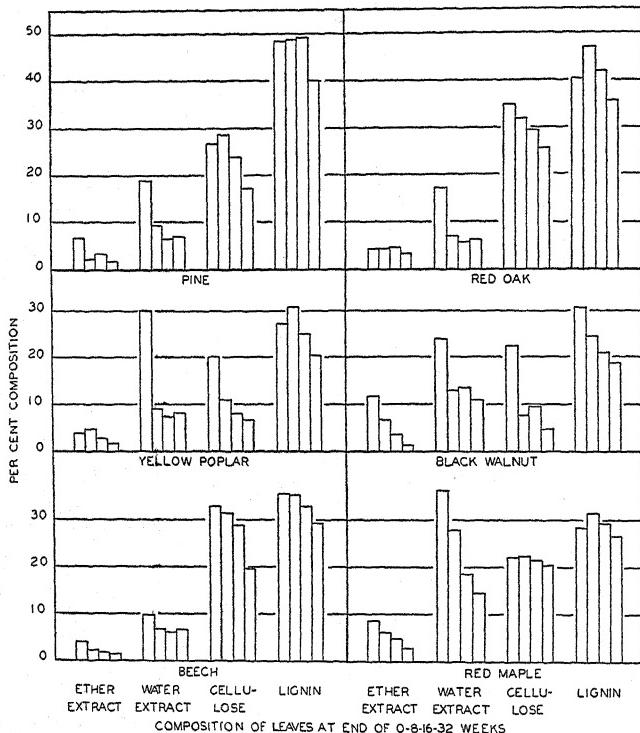
FIG. 4. CHEMICAL CHANGES DURING DECOMPOSITION OF LEAVES
Frequency rectangles represent successive 8-week intervals

Water-soluble material was the most actively attacked constituent of the leaves. The transformation of this fraction occurred most vigorously during the early stage of the decomposition period. A large part of this material was undoubtedly sugars or sugar-yielding substances. The residual water-soluble material, left after the initial active decomposition, was markedly resistant to further changes by microorganisms.

Of the various leaves tested, the greatest losses of water-soluble matter occurred in yellow poplar and red maple, where the total losses amounted to 21.8 and 20.0 gm. of the test samples respectively. This is equivalent to 72.5 and 57.1

per cent of the original water-soluble matter present in each sample. Black walnut, pine, and red oak contained a smaller amount of water-soluble material, and in each instance more than 50 per cent of it disappeared. Beech leaves contained the smallest amount of this fraction (10 per cent), of which only 12 per cent was destroyed.

Cellulose decomposition occurred in varying degrees in all of the leaves. The greatest total loss took place in black walnut (17.6 gm.), beech (13.5 gm.), and yellow poplar (12.8 gm.). Somewhat smaller losses were obtained with pine (9.4 gm.), red oak (8.7 gm.), and red maple (2.0 gm.). Pine and red maple leaves showed slight increases in the cellulose-reacting fraction during the first 8 weeks of the experiment.

Lignin decomposition occurred in all the leaves tested. The rate of decrease was slow, and the amount lost by the samples varied. Black walnut showed a total loss of 11.6 gm. during the 32-week period. Pine and yellow poplar were next, with losses of 8.4 and 7.2 gm. respectively. Beech and red oak showed a still smaller decrease, amounting to 5.8 gm. in the former and 4.9 gm. in the latter. The least decomposition of lignin (1.5 gm.) occurred in red maple.

In all but one instance, namely black walnut, there was a definite initial resistance to the decomposition of lignin. In fact, an apparent synthesis of lignin occurred in the red oak, yellow poplar, and red maple. Similar increases have been noted, in other experiments, with black walnut and beech. In all instances the increase was obtained during the first 8 weeks. This was followed by a slow decomposition of lignin during the remainder of the test period.

Interrelationships of factors

Inasmuch as the measurements made were for the most part of group effects, one cannot expect a very high degree of correlation between the various factors. General correlation was evident, however, in some instances.

A direct relationship between pH and bacterial numbers has been reported by Bokor (1) and by Feher and Vagi (6). A similar relationship in the early stages of decomposition was apparent in this experiment. The samples of beech, red oak, black walnut, and yellow poplar, all of which had initial reactions above 5.0, showed a rapid increase in bacterial numbers during the first week of the experiment. Following the rapid initial activity of bacteria, the numbers declined even though the pH continued to rise. This decline was undoubtedly caused by a decrease in the readily available energy material, since the data on decomposition show that a large part of the water-soluble material was quickly destroyed. Low bacterial numbers in pine and red maple for the first 8 weeks were associated with high acidity. During this period the release of bases, primarily by fungi, raised the pH of pine to about 4.5, which was apparently sufficient to favor bacterial development. In red maple both pH and bacterial numbers increased slowly and were lower than in any of the other samples during the entire period.

The data show that, irrespective of type of flora, the early decomposition affected principally the water-soluble portions but that some of these were rela-

tively stable or were being continually produced as a result of the break-down of more complex constituents. Under natural conditions there is considerable leaching of this water-soluble material into the mineral layers of soil below. These soluble organic salts and acids or bases will profoundly affect the reaction of the mineral soil. This in turn will affect the types of microorganisms which are present in this layer and which may further inoculate new deposits of litter. Thus, whereas in this study all leaves were inoculated with the same types of organisms, under forest conditions there may be a wide difference in the microflora present.

The data in table 1 show a general relationship between final reaction and the amount of decomposition of the original cellulose and lignin. Since there was little change in the relative order of the reaction of the various leaves during the experiment (and none after 8 weeks) it appears that the decomposition of these fractions is accomplished principally by organisms which are sensitive to acid conditions. The one exception to the general rule is red oak, which decomposed more slowly than pine even though it was less acid. Figure 2 shows that

TABLE 1

Decomposition of cellulose and lignin in relation to reaction

LEAF SAMPLE	ORIGINAL CELLULOSE DECOMPOSED	ORIGINAL LIGNIN DECOMPOSED	FINAL pH
	per cent	*per cent*	
Black walnut.............................	81	40	9.4
Yellow poplar...........................	65	26	9.0
Beech....................................	42	17	7.3
Red oak..................................	20	12	6.8
Pine.....................................	37	17	5.7
Red maple...............................	9	7	5.2

this sample had a relatively low fungus population throughout the entire experiment. On the other hand, red maple, with a high content of fungi but a low bacterial population, lost little of its cellulose or lignin. It appears, therefore, that most rapid decomposition of cellulose and lignin occurs when both bacteria and fungi are abundant.

It is definitely known that the decomposition of these fractions cannot be brought about by all microorganisms, but is the result of attack by specific groups of organisms. The presence of cellulose-decomposing bacteria, noted in black walnut and yellow poplar during the latter stages of the experiment, was undoubtedly partly responsible for the rapid decomposition of cellulose in these two samples. Since a fairly large number of other bacteria and fungi may attack cellulose, however, it is not possible to correlate either the presence of any specific group of organisms or the total numbers of all microorganisms with the rate of cellulose decomposition in these mixed cultures.

Experiments by Falck (4, 5) indicate that various species of fungi may act on leaf litter in two ways: first, "by decomposing the cellulose and leaving a lignin rich residue" or, second, "by decomposing cellulose and lignin simultaneously."

Although Falck's experiments were conducted with Basidiomycetes and are not directly applicable here, it appears that in all the samples, except red maple, cellulose was attacked much more readily than lignin by the organisms present. The high acidity of red maple may have been responsible for the low rate of activity of cellulose-decomposing organisms.

The work of Broadfoot and Pierre (3), previously referred to, emphasized the relationship between acid-base balance and decomposition. Although no accurate record of percentage decomposition could be kept, the decomposition of the various fractions which were determined appears to support this view. It is of further interest to note that the samples having a low rate of decomposition are high in lignin. Actually a comparison of acid-base balance with lignin, as given in table 2, shows some relationship between these two properties.

TABLE 2

Relationship between excess base and lignin content of leaves

LEAF SAMPLE	EXCESS BASE	LIGNIN
	m. e./ 100 gm.	*per cent*
Pine	47.9	48
Red oak	70.6	40
Beech	79.4	34
Red maple	88.8	28
Yellow poplar	161.3	27
Black walnut	188.8	30

DISCUSSION

The present investigations are merely an introduction to the study of the effect of microorganisms on the decomposition of forest litter. Since they have been conducted under controlled conditions, they do not necessarily represent the same changes which would take place in the forest. Variations in temperature under natural conditions undoubtedly influence rate and type of decomposition as well as the flora developed. Likewise, leaching will affect the reaction and decrease the amount of decomposition of soluble materials in the humus layer. The study of changes under controlled conditions is necessary, however, in order to separate the effects of the various factors on decomposition.

Although the data are by no means conclusive, they indicate that the type of forest humus developed may be the result of both the rate and the type of decomposition. Leaves with a low content of excess base and a high content of lignin and other relatively stable organic compounds will decompose slowly and tend to produce a mor type of organic layer. The fact that the decomposition of the lignin and cellulose fraction varies in the different species would indicate that under certain conditions the decomposition of these fractions can be enhanced. Thus, even when these are present in relatively large quantities, it may be possible to alter the type and rate of decomposition which occurs. The evidence in table 1 indicates that this is associated with the reaction. It would be expected, therefore, that soils with a high pH would tend to produce mull, and soils with a low pH would tend to produce mor. This

relationship has been noted (11). Furthermore, the type of decomposition in red maple appeared to be different from that in the other samples. In all but the red maple sample the cellulose decomposition was about twice as great as the decomposition of lignin, whereas in the red maple sample, although both fractions decomposed slowly, the percentage decomposition was about the same. The residue from red maple would, therefore, be relatively high in both lignin and cellulose, whereas the residue from other samples would be high in lignin. These would, therefore, give different humus layers.

SUMMARY

Ground leaf samples from six species of trees were inoculated with a soil suspension from a mixed forest stand, incubated for 32 weeks, and changes in flora and in chemical composition noted. The leaf samples were taken from table mountain pine, beech, red maple, red oak, yellow poplar, and black walnut trees.

The results may be summarized as follows:

The pH of all leaves increased during the incubation period. At the end of the incubation period the black walnut had the highest pH, followed in order by yellow poplar, beech, red oak, pine and red maple.

Rapid increases in bacterial numbers were associated with pH, the black walnut showing the most bacteria and red maple the least in the early stages of decomposition. Following the initial increase in bacterial numbers and the decomposition of water-soluble material, there was little evidence of relationship between bacteria and reaction.

Numbers of fungi increased rapidly in all samples regardless of pH.

The types of microorganisms were found to be the same regardless of the kind of leaf sample used.

The early decomposition affected principally the water-soluble materials, whereas some decomposition of cellulose and lignin occurred in the later stages.

The extent of lignin and cellulose decomposition appeared to be associated with pH, the higher rate of decomposition occurring at higher pH values.

An increase in lignin content of red oak, yellow poplar, and red maple occurred during the first 8 weeks of the experiment.

There appeared to be some relationship between lignin and excess base content.

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BOOKS

Ecological Crop Geography. By KARL H. W. KLAGES. The Macmillan Company, New York, 1942. Pp. 615, figs. 108. Price, $4.50.

The book is divided into four parts, of which the first deals with the human factor; the second, with factors of plant physiology; the third, with crop ecology; and the fourth, with the actual distribution of the important crop plants, particularly in the United States of America. Every worker in the field of crops and soils, and especially those engaged in the actual production of crops, will find much of interest and value in the book. An important feature is the extensive bibliography, which gives the reader a comprehensive view of the literature of this field.

Industrial Waste Treatment Practice. By E. F. ELDRIDGE. McGraw-Hill Book Company, Inc., New York, 1942. Pp. 401, figs. 79. Price, $5.

A timely book on the problems involved in the control of pollution of river waters by sewage and industrial wastes. The several chapters deal with the characteristics of these wastes, the treatments employed in their removal, and the nature of the sludges that are recovered. Specific attention is given to wastes from the beet-sugar, milk-product, canning, tanning, paper-mill, textile, meat-packing, laundry, metal, gas, coke, fermentation, and oil industries and to combinations of such wastes with domestic sewage. The book is of especial interest to those who are concerned with the utilization of sewage and factory sludges as soil-improving agents and as substitutes for animal manures.

Liebig and After Liebig. Edited by FOREST R. MOULTON. American Association for The Advancement of Science, Washington, D. C., 1942. Pp. 111. Price, $2.

A symposium of papers presented before the Sections of Chemistry and Agriculture of the American Association for the Advancement of Science at Philadelphia on December 30, 1940. This was in commemoration of the hundredth anniversary of the publication of Liebig's *Organic Chemistry in its Application to Agriculture and Physiology.* The contributors were Arnold K. Balls, Richard Bradfield, Charles A. Browne, Harry A. Curtis, Paul E. Howe, Henry R. Kraybill, Burton E. Livingston, Hubert B. Vickery, and Selman A. Waksman. As the title indicates, the speakers dealt not only with Liebig's scientific contributions but with the progress in those fields of agricultural chemistry in which Liebig pioneered. A most interesting volume by the reading of which one is impressed both as to the science which Liebig knew and that which he did not know.

Methods of Plant Breeding. By HERBERT K. HAYES and FORREST R. IMMER. McGraw-Hill Book Company, Inc., New York, 1942. Pp. 432, figs. 37. Price, $4.

An attractive presentation of the problems involved in plant breeding and of the methods employed in their solution. Pureline, hybridization, and back-cross methods are considered in detail, as is also the breeding of plants for disease and insect resistance. The present status of corn breeding has been reviewed in detail. Other chapters deal with inheritance in wheat, oats, barley, and flax, and with field-plot technique. Every student of this subject will want a copy of this book.

Plant Life. Second Edition. By D. B. SWINGLE. D. Van Nostrand Co., Inc., New York, 1942. Pp. 457, figs. 295. Price $3.

An attractive presentation of plant science in which advantage is taken of the reader's natural interest in life processes rather than in plant structures. The second edition goes a step farther in this direction by introducing more natural history. The illustrations are especially interesting and instructive. The book should be a useful addition to the library of every worker in this field.

Sampling Methods in Forestry and Range Management. By F. X. SCHUMACHER and R. A. CHAPMAN. Bulletin 7. Duke University School of Forestry, Durham, North Carolina, 1942. Pp. 213, figs. 26. Price, $2.

Administrative decisions pertaining to the management of forests often rest upon estimates of the number or condition of the trees. Such estimates involve some type of sampling procedure. This procedure must be such that the error of sampling can be assessed, and the best estimate can be made that is consistent with the time and funds available. The authors apply mathematical statistics to this problem. The bulletin will be of interest to all those who deal with sampling procedures, no matter what their field of research may be.

Soil Science Society of Florida Proceedings. Vol. 2. The Soil Science Society of Florida, R. V. Allison, Sec.-Treas., Gainesville, Florida, 1940. Pp. 146.

Report of an interim meeting of the society held at Tampa, April, 1940, and containing most of the papers presented there and at the regular meeting at Gainesville. The Tampa meeting was a symposium on "Soil Reaction As a Basis for Certain Land Management Practices." At the Gainesville meeting two symposia were held, the first dealing with trace elements and the second with organic matter. Dr. H. H. Bennett and Dr. Selman A. Waksman were guest speakers.

Soil Survey of Puerto Rico. By R. C. ROBERTS. U. S. Department of Agri-culture Bureau of Plant Industry, 1942. Pp. 503, figs. 145, maps 6. Price $3.25.

A detailed survey of the soils of Puerto Rico by the U. S. Department of Agriculture in cooperation with University of Puerto Rico Agricultural Experiment Station. The report includes information on the population of the island, its mineral resources, climate, agriculture, adaptability of soils to crops, productivity ratings, and the morphology and genesis of the soils in relation to

rainfall (varying between 20 and 160 inches), to relief, to vegetation, and to parent rock. Nearly every one of the important zonal, intrazonal, and azonal soil groups occurring in the United States is represented in one or more soil series in Puerto Rico.

Soybeans. By EDWARD JEROME DIES. The Macmillan Company, New York, 1942. Pp. 122. Price, $1.75.

A popular treatment of the history of the soybean, its introduction into the United States, its growth in acreage in this country, and the uses to which the beans are now being put. The book deals especially with the men who have played the most prominent parts in the development of the soybean industry in America and tells an exciting story about this highly important crop.

Symposium on Clay. By RALPH E. GRIM, STERLING B. HENDRICKS, HANS F. WINTERKORN, W. P. KELLEY, and F. H. NORTON. The Journal of Geology, Vol. L, No. 3, pp. 225–330, April–May, 1942. Price, $1.

A series of five papers presented by request at the Fiftieth Anniversary Celebration of the University of Chicago, September, 1941. The complete set of papers presents a highly interesting and instructive summary of the modern concepts of clays. Suggestions are offered with reference to the application of the knowledge gained from the study of clays in agriculture, ceramics, and engineering.

Weeds. Reissue. By W. C. MUENSCHER. The Macmillan Company, New York, 1942. Pp. 579, figs., 123. Price, $4.50.

This book deals with the identification of some 500 weeds and gives suggestions for their control. The present volume is a reissue under a new format. About the only change in content from previous issues is the inclusion of 48 new references, which are appended to the original list. The volume contains the type of information that the field agronomist requires in dealing with this difficult problem.

THE EDITORS.

THE COMPOSITION OF SOIL COLLOIDAL CLAY

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The study of the composition of soil colloidal clay or of the colloidal "weathering complex" meets with difficulty mainly because of the lack of uniformity of the material. In mineralogical studies, for example, one of the chief sources of error is the diversity of the material. This is true in some degree also for chemical and thermal analyses. The inadequacy of the results becomes particularly apparent when such mixtures as the colloidal fraction of clay isolated from soil in the course of its mechanical analysis are investigated. The application of the x-ray method to such a mixture also leads to erroneous conclusions and apparently can give only a very superficial idea of the mineralogical composition and the proportion of the individual components of the colloidal clay.

On the other hand, the study of colloidal clay is essential to the solution of a number of problems in soil science. At present, only provisional information is available regarding the clay minerals composing soil. In this respect one can but second the opinion of Robinson (21), that the study of the clay-mineral components, which characterize the chief groups and subgroups of soils, must be the task of the immediate future. Whatever the trend of the soil-forming process, it is to be expected that besides the characteristic minerals of clay, or a characteristic group of these minerals, inherent in one or another soil type, accessory products of weathering must exist. The role of these accessory products seems to be most important, for their presence determines the properties of the colloidal soil complex. The accumulation of these "contaminations" may give a clearer idea of the alterations due to the soil-forming process and may serve for a more precise evaluation of the stages of development of a given type of soil than the mere determination of the chief groups of typical minerals. Particular significance, in this respect, is attached to the quantitative determination of these "contaminations" and to their relation to the chief groups of clay minerals in the colloidal complex.

Colloidal clay may contain, as such "contaminations," sesquioxides and free silica, clay minerals belonging to definite groups, as well as other clay minerals, the nature of which is obscure. Synthesis experiments show that even under similar conditions, the formation of one mineral gives rise to a small amount of another (19).

Of late, much attention has been paid to the expression of the composition of colloidal clay in the form of the molecular silica-sesquioxide ratio $(SiO_2 : Al_2O_3 + Fe_2O_3)$. Without denying the significance of this ratio, one can envision further progress in the search for methods of dividing colloidal clay into fractions and in the study of the properties of individual fractions. The

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influence of climate on soil formation is reflected by the changes in the composition of soil. These changes are most marked in the colloidal complex. Even in those cases in which the process of weathering is most clearly manifested, as, for example, in podzolization, it is not yet clear whether there is merely an accumulation of sesquioxides in the illuvial horizon of podzolized soils, or whether a more complicated process of weathering, influenced by forest vegetation, takes place, as is assumed by Bogoslovsky (4). It can hardly be a gross mistake to assume that a definite regularity in the distribution of the clay minerals and of the "accessory products" of weathering plays a part in the development of the properties of every soil group.

CLAY FRACTIONATION

Colloidal clay isolated from a soil or a rock rarely is uniform in its mineralogical composition. Besides the main minerals, it includes other minerals that may constitute a considerable part of the clay.

As far as we know, the first clay-fractionation experiments were made by Schloesing. In his note on the composition of clays (23), Schloesing describes the operations which preceded his chemical analyses of kaolins and which consisted in subjecting the kaolin rock to dispersion in water, letting the substances decanted from the precipitations stand in a very weak HCl solution, washing them, and subsequently dividing them into layers by the use of slightly ammoniacal distilled water. Besides these operations, Schloesing applied two triturations: one, after the decantation, for coarser particles; the other, for the finer ones. The results of such a separation of one "exceptionally pure" sample of kaolin were most interesting. After the precipitation of fraction d, which took 27 days, fraction e remained in suspension. After the coagulation of this suspension, the precipitate, which weighed 0.55 gm., occupied a volume of 146 cc. When filtered and dried over $CaCl_2$, it took the form of a thin crust, slightly transparent and strongly adhering to the porcelain. Cohesion, which was almost absent in the coarser fractions, was very pronounced in the clay. From these indications, Schloesing concluded that the sample contained, in addition to kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), a small quantity of colloidal clay (1.4 gm. per 100) containing less Al_2O_3 and more SiO_2 and characterized by a high content of K_2O (4.25 per cent).

Van Bemmelen (3) considered the weathering complex as consisting of two fractions: component A (allophanoids), soluble in concentrated HCl and having a molecular ratio of $SiO_2 : Al_2O_3$ between 3 and 6; and component B (approaching kaolin), soluble in concentrated H_2SO_4 and having a molecular ratio of $SiO_2 : Al_2O_3$ between 2 and 3. Component A is not analogous to Schloesing's "colloidal clay." Its composition is not strictly defined, and it possesses a marked adsorption capacity. The method of Van Bemmelen was recently applied by Hissink, Van der Spek, and Hooghoudt (13) to the investigation of Dutch soils.

Much attention has been paid of late to the study of the chemical composition of colloidal clay isolated from different soils. The conclusion to be drawn from

most of these analyses is that the composition of the clay fraction deviates from that of kaolin. Some attempts to separate soil colloidal clay by means of fractional coagulation were made by Robinson and Holmes (22). Clay suspensions isolated from soil were evaporated; most of the suspension coagulated, but some of the material remained in suspension. Chemical analyses of the coagulated part and of the part remaining in suspension showed no essential differences. Separation by this method does not, therefore, seem feasible.

Drosdoff (8) applied the method of differential coagulation for the same purpose of separation. The suspensions were saturated with Na and Ba ions. The Na-suspensions were treated with dilute NaCl solution in order to coagulate only part of the suspension. Another experiment consisted in centrifuging both Na- and Ba-suspensions and partly precipitating them. Chemical analyses of the coagulated and noncoagulated parts of the suspensions and of the precipitated and unprecipitated parts gave similar results, showing that separation by this method is not feasible either. Somewhat later, Truog and Drosdoff (26) proposed methods by which the accessory minerals could be determined, and found that the composition of the remaining mineral was of the type $R_2O_3 \cdot 4SiO_2$.

Segregation of "contaminations" in the form of sesquioxides and silica that are not an integral part of the mineral lattice can be accomplished with the aid of Tamm's reagent (25). Another method of eliminating the oxides of iron and aluminum with the help of peptization by means of a hydrous sol of SiO_2 was proposed by Fodor and Reifenberg (10). The SiO_2 sol is prepared according to Graham's method. The control experiments of Krassenskaja (15) show that the hydrous sol of SiO_2 does not destroy the minerals of clay, such as nacrite, but decomposes allophanoid clays.

Another method, proposed by Tyulin (27), for separating soil colloids qualitatively, that of fractional peptization, is likewise unsuitable, for both thermal and x-ray examinations have consistently shown that the composition of various groups of gels isolated from Middle Asian clay samples is uniform.

The best guide for the research worker, in the study of the mineralogical composition of the colloidal fraction of clay, is the fact that this composition depends on the size of the colloidal particles. The cause of this dependence may be seen in the prevailing trend of the process of weathering. Physical weathering, that is, the progressive reduction in the size of particles without change in composition, continues to a definite limit. Beyond this limit, reduction in particle size is accompanied by a change of composition; that is, chemical weathering becomes prevalent.

The possibility of separating the colloidal fraction of clay into its components on the basis of particle size has been demonstrated by Schloesing (23). Bray (6) recently reached the conclusion that the colloidal fraction of soil is represented by minerals of varying particle size and is composed chiefly of a mixture of sericite-like and beidellite-type minerals. The largest particles of the colloids $(1 - 0.1\mu)$ are quartz and the sericite-like mineral; the smallest ($<0.06\mu$), the mineral of the beidellite type. Bradfield (5), however, could not detect any

essential difference between the suspensoid $(1.2 - 0.4\mu)$ clays. Marshall (17, 18), in his microscopic study of the individual fractions from $(1\mu$ to 50 m$\mu)$, obtained by means of centrifugation, was unable to detect the presence of a homogeneous material in every case. The cause of these discrepancies seems to be the prevalence, in many instances, of some one mineral in the composition of the colloidal fraction of clay, together with certain associated "contaminations."

EXPERIMENTAL

The method proposed here is based on the characteristic behavior of the several components of colloidal clay; in particular, *on the ability of a certain part of the suspension to form an oriented structure possessing the property of double refraction*. This property is manifested in the most marked degree after elimination of the contaminations (24). If sufficient care has been taken to purify the material with the aid of Tamm's reagent, a part of the clay remains in suspension, while another settles to the bottom of the container in the form of a gel-like precipitate showing a characteristic structure under the microscope. This is the so-called "rodlike" structure, which has a cylindrical shape with rounded ends. The rods are extinguished between the nicols along their long axis. They are optically homogeneous and show positive double refraction (24).

Preliminary experiments on kaolin from Schneeberg (Saxony), Zhuravlin halloysite, and montmorillonite (Crimean "kil") showed that the method had no destructive effect on the mineral clay lattice.

Technique of fractionation

Colloidal clays isolated from a number of parent rocks belonging to Quaternary depositions of the Russian plain[2] were saturated with Na ions and elutriated in distilled water. The suspension was collected and dried first on a water bath to a more concentrated state, then in the oven at about 35°C. The material was shaken with oxalate solution, consisting of 0.1 N $Na_2C_2O_4$ and oxalic acid (8), in the proportion of 1 gm. of clay to 500–600 cc. of solution, until a marked color change was attained; this was accompanied by the dissolution of iron oxides and the peptization of clay substance. A sediment, formed simultaneously with peptization, was separated from the suspension by decantation and was again treated with oxalate solution *until the liquid above it became clear*. This precipitate is designated as fraction C, which manifests under the microscope the characteristic rodlike structure. After treatment with oxalate solution, fraction C is extracted with a 2 per cent solution of Na_2CO_3 to eliminate silica.

Sometimes, in the course of the treatment of clay with oxalate solution, a precipitate is formed, which is gradually peptized. Microscopic examination of such precipitates showed no development of rodlike structure. The substance forming these precipitates was regarded, therefore, as belonging to fraction B and was combined with the rest of the suspension.

In some cases, after the precipitates consisting primarily of fraction B were

[2] The rock samples were supplied by G. F. Mirchink.

peptized, a minute quantity of the material remained, which was not peptized but which did not show the rodlike structure. To distinguish this material from fraction C, it was designated as conditional C.

Fraction B consists of the suspension of clay substance decanted from fraction C and of all the waters used for washing fraction C. Thus fraction B is mixed with fraction A, containing dissolved sesquioxides and silica. To separate these two fractions, the suspension containing both is coagulated by means of saturated NaCl. The precipitate formed contains fraction B; it is separated from the solution of sesquioxides by decanting and is washed free of sesquioxides with 0.05 N HCl (i.e., until the tests for ferric and ferrous ions are negative). It is then extracted with 2 per cent Na_2CO_3 to eliminate silica. Thus we obtain fraction B-A, free from sesquioxides and silica. Both precipitates, i.e., the one containing fraction C and the one containing B-A, are purified by dialysis, dried in the oven at a maximum temperature of 35°C., and analyzed.

Fraction A consists of an oxalate solution of sesquioxides decanted from fraction B following the latter's coagulation with NaCl solution, of the wash-water obtained in the treatment of fraction B with 0.05 N HCl, and of the liquid obtained by the extraction of precipitates C and B with 2 per cent Na_2CO_3 solution. This entire solution is evaporated in porcelain dishes on the water bath, oxidized with a small amount of bromine, and precipitated by a slight excess of ammonia. In these experiments, usually a double precipitation was carried out. After this precipitation the sesquioxide hydrates were not separated from the liquid, which was allowed to stand; but to avoid the loss of colloidal silica, both liquid and sediment together were carefully transferred into cellophane bags for dialysis. After dialysis, the liquid was evaporated on the water bath, and the residue was analyzed.

Determination of mineralogical composition

The investigation of such finely dispersed rocks as clay is beset with great difficulties. For this reason, our knowledge of this material was, until recently, very limited. The application of microscopic methods to the particles of clay minerals usually forming the fraction $<2\mu$ does not give positive results, since the particles are too small for optical identification. Not until x-ray investigations, in addition to optical, chemical, and thermal methods, were applied to the study of clays, did our knowledge actually begin to develop.

With the application of the x-ray method to the study of monomineral clays, however, new difficulties arise. Their cause lies in the complex character of the structure of clay minerals, the dimensions of the elementary cells of which differ but slightly along the two coordinate axes. As a result, their x-ray diffraction patterns show lines with almost similar values for interplanar spacings, and their overlapping—in the case of polymineral clays—is a serious difficulty to the identification of the minerals.

A more precise analysis of polymineral clays demands accurate preparation of the material, involving mechanical methods of fractionation for the purpose of enriching one or another of the fractions with some component of clay. Judged by the works of Marshall (17, 18), Urbain (28), and Antipov-Karataev

and Brunovsky (1), the methods employed for the separation of materials with particles $<2\mu$ do not provide monomineral fractions. In analyzing Na-suspensions of clays, therefore, we applied a preliminary chemical treatment of the material, which led to its fractionation.

Clay minerals have been the object of searching investigations by a number of authors. Thanks to these, only three groups of clays, all of which have been studied in great detail, are now recognized. These are the kaolinite, halloysite, and montmorillonite groups. The group of mica-like minerals has been studied less thoroughly, and the group of clay minerals containing much Mg, still less thoroughly. The works on clay minerals published before 1937 have been reviewed completely by Engelhardt (9), and the latest classification of these minerals is the one proposed by Noll (19).

TABLE 1

Depth, origin, geoglogical age, and color of rocks dispersed as clay

DESIGNATION OF MATERIAL	DEPTH OF BEDROCK	ORIGIN OF SAMPLE	GEOLOGICAL AGE	COLOR
	m.			
1. Covering clay	1.8	Toida (north of Boguchary)	After Riss	Yellow-brown
2. Loess-like loam of the thickness of a syrt stratum	....	Village of Kuro- iedovka	Riss	Light yellow, brownish
3. Covering loam	....	Chirikovo	After Riss	Yellow-brown
4. Fluvio-glaciary loam	....	Village of Kobeliaky (near Orsha)	Würms	Yellowish red
5. No. 191, fluvio-gla- ciary loam	....	South of Sieno	Würms	Yellow-brown
6. Sandy-loam bottom moraine	1.5–2.0	Village of Ukholody (south of Boris- sov)	Riss	Red

Table 1 presents data characterizing the clays, suspensions of which were studied. It shows the designation, depth, origin, geological age, and color of the rocks. Table 2 shows the fractions of Na-suspension of clays that were analyzed. The results of the chemical analyses[3] are summarized in table 3.

The curves of differential thermal analysis[4] are shown in figure 1, and the maxima of the thermal peaks of the curves are summarized in table 4.

The x-ray investigation of the samples was performed[5] according to the method of Debye. Copper and iron radiations from a tube of the Hadding type, operating at a maximum of 30–40 kv. and a current of 7 milliamperes, were employed. The exposures varied between 15 and 30 hours. The diameters of the cassettes of the cameras used were 57.3 mm. and 68 mm. The correction introduced in establishing the real angle of diffraction was based

[3] The analyses were made by M. L. Raphael and T. M. Kozlova.

[4] Obtained on the apparatus of Saladin Le Chatelier, at the Institute of Applied Mineralogy.

[5] At the Institute of Fertilizer and Soil Science.

on the x-ray diffraction pattern of fraction C of Sieno clay + NaCl. The intensities of the lines were evaluated approximately and classified according to the scale: very strong, strong, moderate, weak, very weak, and very very weak.

TABLE 2

Fractions of the Na-suspensions of clays

FRACTIONS	TOIDA	KUROIEDOVKA	CHIRIKOVO	KOBELIAKY	191	UKHOLODY
C	+	+	−	−	−	+
B-A	+	+	+	+	+	+
A	+	+	−	−	−	−
B	+	−	−	−	−	−

TABLE 3

Chemical analyses of Na-suspensions and of fractions of clays

	TOIDA INITIAL SUSPENSION	KUROIEDOVKA INITIAL SUSPENSION	CHIRIKOVO INITIAL SUSPENSION	KOBELIAKY INITIAL SUSPENSION	191 INITIAL SUSPENSION	TOIDA FRACTIONS C	TOIDA FRACTIONS B-A	KUROIEDOVKA C	CHIRIKOVO B-A	KOBELIAKY B-A	UKHOLODY Conditional C	UKHOLODY B-A	191 B-A	TOIDA A	TOIDA B	GRIM'S SERICITE-LIKE MINERAL
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
SiO_2	49.18	50.85	49.72	48.54	49.14	52.58	53.34	53.74	53.13	49.63	42.61	52.35	50.46	3.04	72.68	50.10
Al_2O_3	21.33	20.69	21.78	22.08	22.35	21.69*	24.69*	23.13*	24.81	23.90*	19.00*	26.22	21.10*	3.00		25.12
Fe_2O_3	10.30	10.37	10.59	8.47	10.43	7.98	4.00	4.26	4.16	5.24	3.53	4.39	4.85	77.52	8.02	5.12
FeO	0.79	0.97	0.86	1.45	0.74	n.d.†	0.89	1.57	n.d.	1.24	..	0.59	1.09	0	..	1.52
MnO	0.72	0.20	0.29	0.27	0.30	0.33	n.d.	0.30	0.24	0.73	..	0.17	0.50	..	..	..
CaO	0.79	1.15	0.45	1.99	1.03	1.23	0.72	1.65	1.19	2.45	11.08	0.76	1.80	..	..	0.45
MgO	3.41	3.49	3.14	3.01	3.13	2.61	2.65	2.49	2.11	2.25	1.72	2.04	2.17	..	..	3.93
K_2O	2.44	2.11	1.34	5.08	3.42	2.44	2.48	1.99	1.98	5.58	..	5.39	2.88	..	..	6.93
Na_2O	0.57	0	1.44	0.28	0	2.17	2.55	0.90	3.89	0	..	0.62	0.93	..	..	0.05
TiO_2	0.61	0.81	n.d.	0.86	n.d.	0.36	0.41	0.30	0.39	0.70	0.79	0.73	0.17	0	..	0.50
P_2O_5	0.17	0.22	0.15	0.19	0.22	..	..	..	..	..	..	0.11	..	..	..	..
Loss on ignition	9.00	8.57	9.79	7.78	9.24	8.66	8.13	8.16	8.95	8.27	..	7.11	10.44	..	..	..
Total	99.31	99.43	99.55	100.00	100.00	100.05	99.86	98.49	100.85	99.99	..	100.48	96.39	..	..	
Bound H_2O	7.90	8.23	6.79	7.38	5.69	..	4.51	..	7.55	6.16	..	..	..	..	..	6.82
Hygroscopic H_2O	8.63	8.68	11.27	4.14	8.00	10.96	11.82	10.14	8.96	4.27	6.21	3.31	7.81	10.86	..	1.90
SiO_2/R_2O_3 molar ratio	2.99:1	3.15:1	2.95:1	2.99:1	2.87:1	3.33:1	3.33:1	3.54:1	3.27:1	3.10:1		3.40:1	3.05:1	3.40:1		

* Determined together with P_2O_5.

† n.d. = not determined.

The values of the interplanar spacings of the investigated suspensions and of their individual fractions, as well as the intensities of the respective lines, are summarized in tables 5 and 6.

The results of the calculations for the x-ray patterns of some of the samples are presented graphically in figure 2, where the interplanar spacings are indicated on the abscissa and the intensities of the lines on the ordinate.

In the preliminary x-ray investigation, it was impossible to determine the clay minerals unequivocally, because lines with interplanar spacings exceeding 4.42 A. could not be obtained on the x-ray pattern with the cameras used.   These patterns showed only that the composition of all the suspensions was very similar.   Every one of the suspensions is represented by the same complex of clay minerals, and they all contain as contaminations insignificant amounts of quartz and iron oxide.   Chemical analyses as well as the thermal curves confirm their close resemblance.

The thermal curves have three common endothermic peaks and one not very marked exothermic peak.   The maxima of the thermal peaks are, on the average,

TABLE 4

Thermal peaks of Na-suspensions and clay fractions

NUMBER	MATERIAL	ENDOTHERMIC PEAKS							EXO-THERMIC PEAKS
		1st	2nd	3rd	4th	5th	6th	7th	
		°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
	Initial suspensions								
1	Toida	115	550						868
4	Kuroiedovka	128	544		800				900
7	Chirikovo	148	545	600	810				870
9	Kobeliaky	115	559		842				900
11	Ukholody	134	560		829				875
12	191	123	541		843				900
	Average..........	127	550		825				885
	Clay fractions								
2	Toida C	154			542	710		800	867
3	Toida B-A	130			544	664			
5	Kuroiedovka C	161			559			800	846
6	Kuroiedovka B-A	131	500			641		828	
8	Chirikovo B-A	146	407		528			800	866
10	Kobeliaky B-A	132	200	418	553	656	750	843	
13	191 B-A	122	200	438	532	618	700	830	888
	Average..........	139			543			817	867

at 127°, 550°, and 825°C.; that of the exothermic peak is at 885°C.   The chemical analysis of the suspensions is very close to that of beidellite.   X-ray patterns of the suspensions in both an air-dry and a swollen condition were prepared on a flat film with a distance of 60 mm. between the object and the film, for the purpose of their identification with beidellite.   The x-ray patterns did not show any lines with a small angle of diffration.   This was considered sufficient grounds for assuming that the clay mineral of our suspensions is not beidellite, since it is known that the latter, like montmorillonite, is characterized by its intermicellar swelling.   The x-ray patterns showed that anauxite was not the chief component of the suspensions.

1 Toida
  initial suspension

2 Toida fraction C
3 " " B-A

4 Kuroiedovka
  initial suspension

5 Kuroiedovka
  fraction C
6 " " B-A

7 Chirikovo
  initial suspensior
8 Chirikovo
  fraction B-A

9 Kobeliaky
  initial suspensior

10 Kobeliaky
   fraction B-A
11 Ukholody
   initial suspension
12 N 191 initial suspension

13 N 191 fraction
   B-A
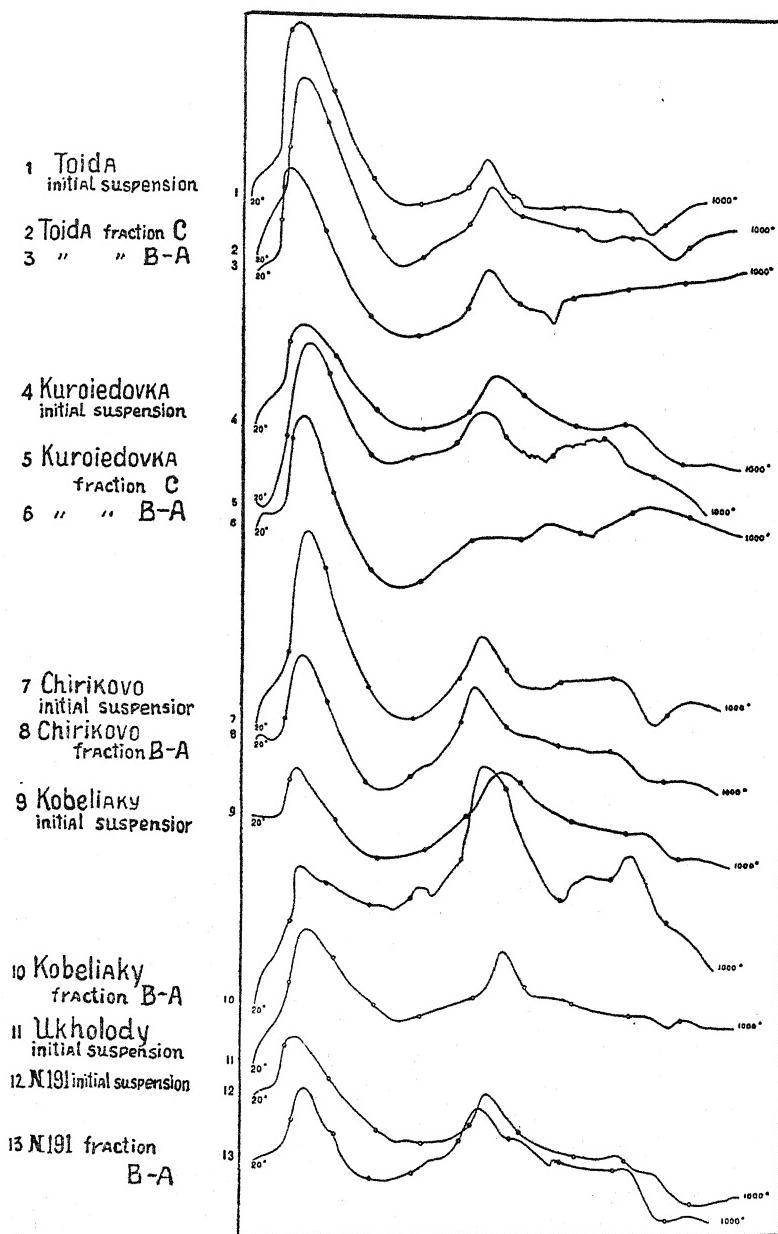
FIG. 1. CURVES OF DIFFERENTIAL THERMAL ANALYSIS OF CLAY SUSPENSIONS AND OF FRACTIONS OF CLAYS

In a further effort to determine the composition of the suspensions, an attempt was made to liberate them from iron oxide contaminations with the aid of oxalate solution.

As a result of the action of oxalate solution on a clay suspension, iron oxides

and aluminum oxides pass into the solution in which fraction B is suspended, and fraction C is precipitated. The chemical analysis of fraction B of Toida clay (cf. table 3) shows that it contains 72.68 per cent of SiO_2 and only 8.02 per cent of R_2O_3. Its x-ray pattern shows the presence of a large amount of amorphous SiO_2 together with a small amount of the same clay complex that was found later in Toida C.

TABLE 5

Interplanar spacings and intensities of x-ray pattern lines* of Na-suspensions of clays

NUMBER OF LINES	TOIDA		KUROIEDOVKA		CHIRIKOVO		KOBELIAKY		191		UKHOLODY		GRIM'S SERICITE-LIKE MINERAL	
	d(hkl)	Intensity	d(hkl)	Intensity	d(hkl)	Intensity	d(hkl)	Intensity	d(hkl)	Intensity	d(hkl)	Intensity	d(hkl)	Intensity
	A.		A.		A.		A.		A.		A.		A.	
1	4.38	s.	4.40	s.	4.40	s.	4.38	v.s.	4.47	s.	4.47	s.	{10.15 / 4.92	4 / 2
2	4.17	v.v.w.	4.16	v.w.	4.17	v.v.w.	4.17	v.v.w.	4.17	m.	4.17	v.v.w.	4.45	5
3	..	..	..		..		..		3.88	v.v.w.	..	..	..	
4	3.50	m.	3.58	m.	3.58	m.	3.45	s.	3.53	m.	3.53	s.	3.67	½
5	3.27	s.	3.33	s.	3.33	s.	3.27	s.	3.33	v.s.	3.33	s.	3.31	m.
6	3.05	w.	3.00	v.v.w.	3.00	v.v.w.	..		3.00	m.	2.99	m.	3.05	½
7	2.79	m.	2.80	v.w.	2.79	v.v.w.	2.79	m.	2.80	w.	2.80	w.	..	
8	2.68	v.w.	2.68	v.v.w.	2.69	v.v.w.	2.69	v.v.w.	2.66	v.w.	2.66	v.w.	..	..
9	2.55	s.	2.55	s.	2.55	s.	2.55	v.s.	2.55	s.	2.55	s.	2.57	5
10	..	..	2.45	w.	2.45	m.	..	..	..	..	..	..	2.47	1
11	2.36	m.	2.37	w.	2.37	w.	2.36	w.	2.38	w.	2.38	v.w.	2.37	2
12	..	..	..	..	..	..	..		..	..	2.24	v.w.	2.25	1
13	..	..	2.18	v.v.w.	2.18	v.v.w.	..	..	2.18	v.w.	..	..	..	..
14	2.12	w.	2.11	w.	2.11	w.	2.12	w.	2.11	v.w.	..	..	2.13	1
15	1.97	m.	1.97	w.	1.97	m.	1.97	s.	1.99	s.	1.95	m.	2.00	1
16	..	..	1.86	v.v.w.	1.86	v.w.	..	..	1.86	v.v.w.	1.85	v.v.w.		
17	1.80	v.v.w.	1.81	v.v.w.	1.81	v.v.w.	1.80	v.v.w.	1.80	v.v.w.	1.81	v.v.w.	..	..
18	1.70	s.	1.69	m.	1.69	m.	1.70	s.	1.69	m.	1.69	m.	1.70	1
19	1.65	s.	1.65	m.	1.65	s.	1.65	v.s.	1.65	s.	1.65	s.	1.64	2
20	1.54	v.v.w.	..	..	1.53	w.	1.53	v.v.w.	1.53	v.v.w.	1.54	v.v.w.	..	
21	1.50	v.s.	1.50	s.	1.50	s.	1.50	s.	1.50	v.s.	1.50	s.	1.50	4

* v. s. = very strong; s. = strong; m. = moderate; w. = weak; v. w. = very weak; v. v. w. = very, very weak.

After the separation of precipitate C and the subsequent treatment of the precipitate and suspension with a 2 per cent solution of Na_2CO_3, fractions A, B-A, and C were obtained.

It must be noted that the suspensions of clays can be sharply subdivided into two types by the quantitative relations of fractions C and B-A. To the first type belong the clays of Toida and Kuroiedovka, in which both fractions are present in measurable quantities. The second type is characterized by the

prevalence of fraction B-A, fraction C being present in an insignificant quantity or completely absent. In the following discussion, this minute quantity of fraction C is designated as conditional C.

What are these fractions and in what do they differ from the original suspensions and from one another? The brownish red color of fraction A of every clay indicates that iron oxide must be the chief component. This is fully confirmed by both chemical and x-ray analyses. Thus, fraction A of Toida shows

TABLE 6

Interplanar spacings and intensities of x-ray pattern lines* of fractions of clays

CHIRIKOVO B-A		KOBELIAKY B-A		UKHOLODY				TOIDA				KUROIEDOVKA				TOIDA B		GRIM'S MICA-LIKE MINERAL	
				Conditional C		B-A		C		B-A		C		B-A					
$d(hkl)$	Intensity	$d(hkl)$	Intensity	$d(hkl)$	Intensity	$d(hkl)$	Intensity	$d(hkl)$	Intensity	$d(hkl)$	Intensity	$d(hkl)$	Intensity	$d(hkl)$	Intensity	$d(hkl)$	Intensity	$d(hkl)$	Intensity
A.		A.		A.		A.		A.		A.		A.		A.		A.		A.	
		10.1	v.w.	10.6	v.w.	..	..											10.15	4
7.15	v.w.	..	..	7.48	v.w.	..	..	7.45	v.v.w.	..	..	7.58†	v.v.w.	7.47†	v.v.w.	..	..	..	..
..	..	..	..	..	..	..	..	..	..	..	..	..	..	5.42	v.v.w.	..	..	4.92	2
4.42	v.s.	4.42	s.	4.40	w.	4.42	s.	4.42	v.s.	4.42	v.s.	4.42	s.	4.42	s.	4.40 ‡	s.	4.45	5
4.00	v.w.	..	..	..	..	..	..	4.02	v.v.w.	..	..	..	..	3.98	v.w.			..	..
3.57	w.	3.50	v.w.	3.57	v.w.	3.60	m.	3.57	v.v.w.	..	..	..	..	3.57	w.	3.57	s.	3.67	½
3.30	m.	3.30	s.	3.34	v.s.	3.34	v.s.	3.30	m.	3.30	m.	3.30	w.	..	..	..	..	3.31	3
2.85	w.	2.86	m.	2.90	v.w.	2.86	m.	2.85	m.	2.85	m.	2.90	v.w.	2.85	v.w.	..	..	..	..
2.57	s.	2.56	s.	2.57	m.	2.56	s.	2.56	v.s.	2.57	v.s.	2.58	s.	2.57	s.	2.57	m.	2.57	5
..	..	..	..	..	..	..	..	2.42	w.	..	..	..	..	..	..	..	..	2.47	1
2.36	m.	2.35	w.	2.35	w.	..	..	..	..	2.35	m.	..	..	2.35	m.	..	..	2.37	2
2.20	v.v.w.	2.21	w.	..	..	..	..	..	..	2.20	w.	..	..	..	..	..	..	2.25	1
2.00	w.	1.97	m.	1.99	w.	2.00	w.	..	..	2.00	w.	1.98	w.	2.00	w.	1.98	w.	2.13	1
..	..	..	..	1.93	w.	..	..	..	..	..	..	..	..	..	..	..	..	2.00	1
..	..	..	..	1.89	w.	..	..	..	..	..	..	1.86	w.	..	..	..	..	..	..
1.80	v.v.w.	1.81	w.	1.83	w.	1.80	w.	..	..	1.83	w.	1.68	s.	..	..	..	..	..	..
1.68	s.	1.66	s.	1.67	m.	1.68	v.s.	1.65	s.	1.67	s.	..	..	1.68	s.	1.65	m.	1.70	1
..	..	..	..	1.62	w.	..	..	..	..	..	..	..	..	..	..	..	..	1.64	2
..	..	..	..	1.54	w.	1.54	w.	..	..	..	..	..	..	..	..	..	..	..	..
1.50	s.	1.50	s.	1.50	m.	1.50	s.	1.50	v.s.	1.50	s.	1.51	s.	1.51	s.	1.50	m.	1.50	4
1.37	v.w.	1.38	v.w.	..	..	1.45	w.	..	..	..	..	..	..	..	..	..	..	..	..
..	..	1.34	v.w.	..	..	1.37	m.	..	..	..	..	..	..	..	..	..	..	..	..
1.30	m.	1.30	m.	..	..	..	..	1.30	m.	1.30	m.	1.35	w.	1.30	m.	..	..	1.30	3

* v.s. = very strong; s. = strong; m. = moderate; w. = weak; v.w. = very weak; v.v.w. = very, very weak.

† A wide, diffuse, hardly discernible ring.

‡ A wide ring with cut-out borders.

77.52 per cent of Fe_2O_3 and only 3 per cent of Al_2O_3 and 3.04 per cent of SiO_2. The x-ray patterns of the same fraction of Kuroiedovka and Chirikovo clays supply a picture of hydrohematite. The comparison of the chemical analyses of the original suspensions with those of fractions C and B-A shows the enrichment of the latter by the following oxides: SiO_2, Al_2O_3, and CaO, and their improverishment in respect to iron oxides. Accordingly, the color of the majority of the fractions is gray or grayish green. The character of the thermal

curves of every suspension and of most of their fractions is identical.   There are
but slight distinctions consisting in a certain displacement of the characteristic
thermal peaks; the low-temperature peak of the fractions shifts in the direction
of higher temperatures, while the others shift in the opposite direction.

For a comparison of the fractions, it was possible to use the suspensions of
Toida and Ukholody clays.   The chemical analyses of both fractions of Toida
clay are very similar, their x-ray patterns are identical, and their thermal curves
are slightly different.   On the other hand, the difference between the fractions of
Ukholody clay is immense.   This difference can be seen readily in the results of
both the chemical and the x-ray analyses.   The chemical analysis of conditional
C shows a lower content of SiO_2 and Al_2O_3 and a higher content of CaO.   The
x-ray pattern of B-A is identical in appearance with that of the fractions of the
clays of the first type, whereas that of conditional C is much more intricate.
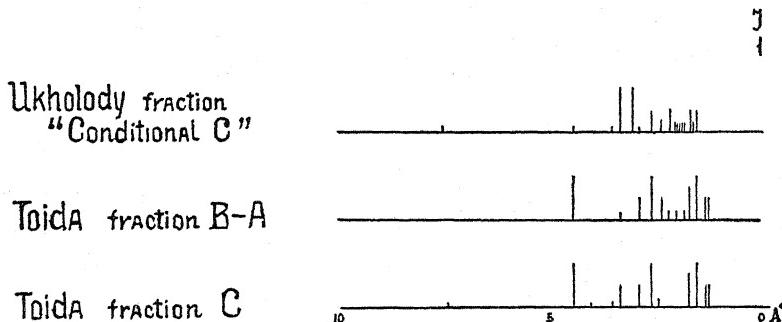
FIG. 2. INTERPLANAR SPACINGS AND INTENSITIES OF X-RAY PATTERN LINES OF SOME
CLAY FRACTIONS

Interplanar spacings in Ängström units, indicated on abscissa; intensities of lines in-
dicated on ordinate.

Since the mineral complex of fraction C of the Toida and Kuroiedovka clays
is found in many colloidal clay fractions and since, therefore, this fraction repre-
sents the purest material, according to the data of x-ray and thermal analyses,
our determination of the mineral complex was made on fraction C.

The x-ray patterns of fraction C of Toida and Kuroiedovka clays supply a
series of intense lines with the following values of interplanar spacing: 4.42,
2.57, 1.66, and 1.50 A.; a line of moderate to weak intensity with $d = 3.30$ A.;
and a number of weaker lines.   This series of intense lines resembles greatly the
line series of montmorillonite, but differs from the latter in the absence of lines
with an interplanar spacing ~ 15 A., the absence of intramicellar swelling, and a
slight difference in their position.

Analysis of the thermal curves and of the results of x-ray investigations lead
to two possible assumptions: first, that Toida is a monomineral; and second,
that it is a polymineral.

Let us determine complex C on the basis of each of these assumptions.   Let
us take for this the chemical analyses of fractions C and find the molecular ratio

of their oxides.   Assuming the molecular content of Al_2O_3 to be equal to 1, we obtain the following stochiometric formula:

$$3.43 \cdot SiO_2 \cdot Al_2O_3 \cdot 0.41 \text{ RO} \cdot 0.18 \text{ RO} \cdot 1.55 \text{ H}_2O + \text{bound } H_2O$$
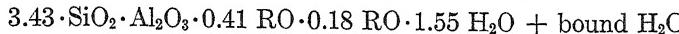
In computing this formula, bound water has not been determined either for Toida C or for Kuroiedovka C; therefore, its value is taken as the average of the loss on ignition of these fractions and of the bound water of fractions B-A of Toida and Chirikovo.   Moreover, the presence of a slight difference in the x-ray patterns of fractions C and B-A of Toida leads to the conclusion that there must be many isomorphous substitutions in this mineral.   Assuming that Fe^{+++} substitutes Al; Fe^{++}, Ca; and Mn, Mg; 3 MgO $\backsimeq$ 2 Al_2O_3 and $H_2O \backsimeq K_2O$, we obtain for our mineral, composing fraction C, the following formula:

$$3 SiO_2 \cdot Al_2O_3 \cdot 0.5(KH)O \cdot H_2O + \text{bound } H_2O$$
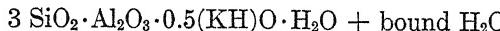
This mineral, in its x-ray characteristics, resembles mineral X described by Hofmann (14) and is related to the sericite-like mineral described by the same author (16), but differs from them in the absence of lines with small angles of diffraction and in the lowering of the intensities of a number of lines (cf. table 6). In its chemical composition and specific gravity it resembles the sericite-like mineral discovered by Grim (11, 12) in the clays and shales of Illinois and is very similar, both chemically and in the character of its thermal curve, to the "monothermite" of Beliankin (2).   This mineral was found recently by Beliankin as one of the components of Chasov-Yar clay and of many other clays of the U.S.S.R. and still earlier, by Zemiatchensky in samples of weathered granite boulders and in samples of slimes (29).   Thus if we assume fraction C to be a monomineral, we come to the conclusion that the chief component of the suspensions of the clays of Quarternary deposition in the U.S.S.R. is a sericite-like mineral.

The characteristics ascribed to this mineral by these investigators are interesting.   Grim and Hofmann characterized it as a mica-like mineral, Beliankin considered it as near the kaolinite group, and Hofmann found a resemblance between its x-ray pattern and that of montmorillonite.   On this basis one might consider that this sericite-like mineral occupies an intermediate position between the groups of kaolinite, mica, and montmorillonite.   Moreover, Hofmann points out that the sericite-like mineral possesses a varying exchange capacity. Both these facts raise doubts as to the existence of such an independent mineral and suggest that we are dealing with a mixed series or with a particular type of a fine mixture of several minerals, i.e., sericite, kaolinite, and a mineral of the same chemical composition as montmorillonite.   Such a mineral has been designated by Fersman as "paramontmorillonite," the designation that will be used in the following discussion.   This mineral, on the basis of the present study, must possess the following characteristics: Its stochiometric formula is $H_2Al_2Si_4$-$O_{12} \cdot H_2O$ + bound H_2O; its x-ray pattern resembles that of montmorillonite, from which it differs, however, by a slight change in parameter C; it shows no

intramicellar swelling and produces a thermal curve having an endothermic peak (near that of kaolinite) with a maximum at 550°C.

On the assumption that all of the potassium oxide belongs to sericite, the percentage composition of the mineral complex of fraction C is calculated to be 33 per cent sericite + 4 per cent kaolinite + 63 per cent paramontmorillonite.

The same complex may be present also in the beidellites and in the anauxites investigated by Orcel (20) with the help of thermal analysis.

It is possible that in the process of weathering of feldspars under the action of CO_2 and H_2O the reaction may go in three directions simultaneously and lead to three products, kaolinite, paramontmorillonite, and sericite:

$$K_2Al_2Si_6O_{16} + CO_2 + 2H_2O = H_2Al_2Si_2O_8 \cdot H_2O + K_2CO_3 + 4SiO_2$$
$$K_2Al_2Si_6O_{16} + CO_2 + 2H_2O = H_2Al_2Si_4O_{12} \cdot H_2O + K_2CO_3 + 2SiO_2$$
$$3KAl\,Si_3O_8 + CO_2 + H_2O = H_2KAl_3Si_3O_{12} + K_2CO_3 + 6SiO_2$$
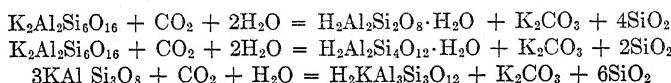
As the result of these reactions alkaline waters wash out some of the liberated SiO_2. Apparently, part of it remains with the other products, and we find it, perhaps, in the form of silica-gel in fraction B of Toida clay.

Thus in the suspensions of U.S.S.R. clay, the prevalent mineral is paramontmorillonite. In its x-ray pattern, therefore, the most distinct lines are those that it has in common with sericite and its own intense lines. Possibly, the prevailing mineral of Illinois clays is sericite, and its x-ray pattern accordingly presents a picture closely resembling mica and possessing an intense line with $d \sim 10$ A. (cf. table 6).

Thus, if we subject the analysis of the sericite-like mineral of Grim (cf. table 3) to a calculation of the foregoing kind, we find that it can be computed as a mixture of ~ 38 per cent paramontmorillonite + 62 per cent sericite. Its specific gravity might serve as a proof of this. We believe that the specific gravity does not differ much from that of mica and must be near 2.47, the value determined by Kerr for one of the mica-like minerals of the United States. If this is correct, the specific gravity of fraction C of Toida and Kuroiedovka must be still lower. The quantity of this substance available was too small to allow the use of a pycnometer. The specific gravity, therefore, was established by means of Tule's[6] liquid, and was found to average 2.46.

It is still impossible to determine the character of the mixture. On the one hand, there are grounds for considering it an isomorphous mixture, the extreme members of which are paramontmorillonite, kaolinite, and sericite; on the other, it may be regarded as a particularly fine stratification of minute crystals of the minerals, the loops of the strata being similar, but their thickness different. Which notion is more nearly correct can be decided only after further investigation of a great number of clays by the complex method with a preliminary treatment of the material to be analyzed.

For determination of the composition of fraction conditional C of Ukholody clay, only x-ray data are available. From these we conclude that, besides the mineral complex of fraction C, it contained calcium, quartz, and muscovite.

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[6] The determination was performed in the mineralogical research laboratory by B. Kariakina.

The chief component of the B-A fractions of all our suspensions is, as already mentioned, complex C. The only exception is fraction B-A of Kuroiedovka, which on the basis of the thermogram, is predominantly montmorillonite. It was impossible to determine precisely the contaminations of this fraction. Only in Kobeliaky could the presence of muscovite, quartz, and kaolinite, besides complex C, be definitely established.

Thus it may be concluded that the chief component of the suspensions of clays belonging to the Quaternary depositions of the Russian plain is a mineral very similar to the sericite-like mineral discovered by Grim and Kerr in clays, which may be regarded as a particularly fine, almost an isomorphous, mixture of paramontmorillonite, sericite, and kaolinite. As contaminations it contains muscovite, quartz, kaolinite, calcium, and hydrated iron oxide.

It is difficult as yet to reach a final conclusion on the proposed method of fractionation, since there remain some obscure points, which can be elucidated only by further research.

DISCUSSION

If the assumption that fraction C is a mixture of sericite, paramontmorillonite, and kaolinite is corroborated by future research, then the optical homogeneity of this formation is a very curious phenomenon. We have had to deal with a phenomenon of this kind when studying clay-humus mixtures (24), which also showed an optically homogeneous structure. Which of the components is the structure-forming factor is still undecided.

The colloidal behavior of fraction C is that of a uniform substance possessing definite properties, characterized primarily by their independence of the kind of absorbed iron. The precipitate representing fraction C of the Na-suspensions is not peptized either by the oxalate ion or by the action of Na_2CO_3 solution. Fraction B-A is similar to fraction C both in structure and in mineralogical composition, but, unlike fraction C, is characterized by a contamination, the nature of which is obscure and the presence of which alters markedly the colloidal behavior of the substance. Montmorillonite (Crimean "kil") possesses a marked swelling capacity, but it loses this capacity when it is purified by treatment with oxalate solution and Na_2CO_3, as has already been indicated. After it was kept in water for about a month, the treated sample of montmorillonite did not show any swelling. The explanation of this phenomenon is to be sought in the marked tendency to aggregation that develops after the elimination of contaminations (24). Cohesion between the particles increases to such an extent that this force proves sufficient to resist peptization and swelling.

If we are to understand the role of iron oxides as that of leveling out the difference in the behavior of fractions C and B-A, we may expect that after the elimination of iron oxides (podzolization) or after their reduction (the process of glei formation), peculiarities in the behavior of fractions C and B-A will be manifested. If, moreover, we take into account the fact that this mineral prevails in the composition of clays of widely varying origin and age, and that in most cases clay is entirely composed of it, the phenomena here described may find application in the explanation of various aspects of the processes of soil formation.

In this respect the role of the contaminating material may be very great. Its accumulation or elimination and in general the quantitative determination and study of its mineralogical composition may serve as a more reliable means of characterizing soil formations than the determination of the main minerals of clay that are present in the soil.

It should be noted that montmorillonite may be present in fraction B-A, as it was in Kuroiedovka clay. We are dealing thus with a limited range of clay minerals, composing the major part of the colloidal clay of the soil. This agrees well with the conclusions of Bray, Clark, and others (6, 7).

The behavior of Kuroiedovka clay, composed of montmorillonite and fraction C, is most curious. The properties of montmorillonite, despite the fact that it comprises about 50 per cent of the initial suspension, are suppressed by fraction C. This is particularly evident in the thermograms of the original material and of fractions C and B-A taken separately (fig. 1). The thermal peak, above 600°, of montmorillonite is displaced toward the 500° peak in the initial suspension, and the thermogram of this material, like that of fraction C, in no way reflects the characteristic features of the thermogram of montmorillonite. From this, one can see that thermal curves, chemical analyses, and x-ray studies all fail to provide reliable information on the composition of the complex clay of soil without fractionation.

SUMMARY

A method for the fractionation of colloidal clay is described, on the basis of which a number of suspensions of clays belonging to the Quaternary depositions of the Russian plain have been studied by x-ray, chemical, and thermal methods.

This study demonstrates that the chief component of these clays is a mineral, of the formula

$$3SiO_2 \cdot Al_2O_3 \cdot 0.5 \ (KH)O \cdot H_2O + \text{bound } H_2O,$$
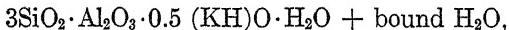
resembling the sericite-like mineral of Grim and Kerr and designated as "paramontmorillonite." In its properties, this mineral occupies an intermediate place between the minerals kaolinite, sericite, and a mineral of the same composition as montmorillonite, but from which it differs in some most important characteristics. The sericite-like mineral studied here is considered as a mixture of ~ 33 per cent sericite + 63 per cent paramontmorillonite + 4 per cent kaolinite. The sericite-like mineral of Grim may be regarded, in turn, as a mixture of ~ 0 per cent kaolinite + 38 per cent paramontmorillonite + 62 per cent sericite.

The character of the mixture, as well as the kind of the mineral designated as paramontmorillonite, may be established only after further study of clays that have been prepared carefully for analysis.

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SOME PHYSICAL PROPERTIES OF THE B HORIZONS OF PIEDMONT SOILS

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In recent years the influence of physical properties of B horizons on soil erosivity has been recognized. More recently the writer has found that physical characteristics of B horizons of soils in the Piedmont Plateau are of marked importance in determining quality of land for timber crops. Physical properties of B horizons which influence soil aeration and movement of water may greatly affect not only plant growth and erosion, but also water infiltration and storage, and rapidity of surface runoff even under forest cover.

Shrinkage and swelling of clay B horizons markedly affect soil aeration and water movement; however, adequate methods for measurement of volume changes in fine-textured soils under various moisture conditions have not been worked out, especially with soils the natural field structure of which has been undisturbed.

In the Piedmont region most residual soils have well-developed textural profiles and the B horizons are usually clays. The clays vary greatly in plasticity, structural characteristics, shrinkage and swelling, water infiltration, and aeration when moist. Examples of differences in clay B horizons are found in the White Store (red phase), Orange, and Tirzah series for which some data on physical properties are included here. The White Store (red phase) series is derived from fine-textured sedimentary rocks of Triassic age. The dark, dull-red B horizon shrinks and swells greatly with moisture changes; it is poorly aerated when moist, very erosive, and a poor site for trees unless the A horizon is of considerable thickness (more than 8 inches). The Orange series is derived from mixed acidic and basic rocks of the Carolina slate formation. Its B horizon is dull brownish yellow and has the physical properties of the White Store. In contrast, the Tirzah series, derived from mixed basic rocks of the Carolina slate formation has a relatively shallow A horizon and a deep, dark-red B horizon, which usually contains more clay than the other two series, but is friable and well aerated, and allows for relatively rapid water movement.

The data given in table 1 were obtained on samples collected in September, 1941. At that time the soil was probably as dry as it ever becomes in this area. "Relative wetness" values of around 30 per cent obtained generally. Because of low moisture content, the soil was at its greatest field density per unit volume.

Undisturbed samples of B horizons were obtained in the field by use of a sampling cylinder[1] with a diameter of 5 inches and a length of 2 inches (fig. 1). The field samples were allowed to soak in water for 2 weeks, at which time the excess soil was removed even with the tops of the cylinder. This excess material,

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[1] Coile, T. S. 1936. Soil Samplers. *Soil Sci.*, 42, 139–142.

TABLE 1

Some physical properties of Piedmont B horizons

SOIL SERIES	1	2	3	4	5
	CLAY (<0.002 mm.)	VOLUME-WEIGHT RATIO	SWELLING	SHRINKAGE	M.E. MINUS X.E.*
	per cent†		*per cent‡*	*per cent§*	
Orange..................	65	1.232	22.1	40.1	28.3
White Store (red phase)...	62	1.292	19.1	40.0	25.0
Tirzah.................	70	1.056	11.4	27.7	10.4

* M.E. minus X.E. = Moisture equivalent minus xylene equivalent.

† Of oven-dry weight.

‡ Of volumes of saturated soil or of cylinder.

§ Of volume of cylinder.
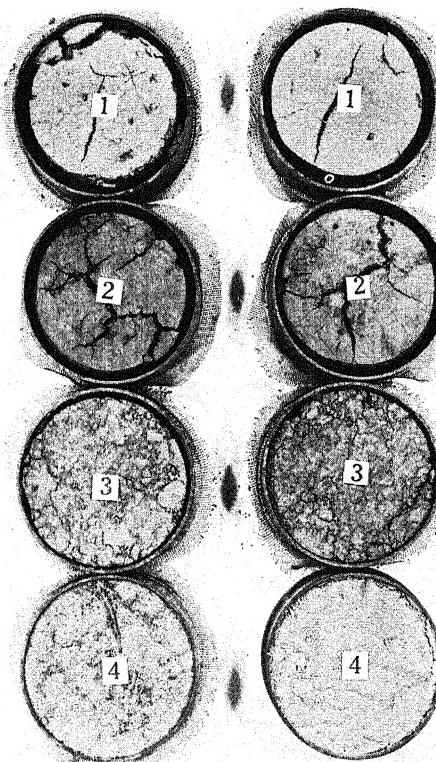
FIG. 1. SHRINKAGE OF SOME PIEDMONT SOILS INITIALLY SATURATED WITH WATER AND OVEN-DRIED AT 105° C.

1. Orange clay; 2. White Store (red phase) clay; 3. Tirzah clay; and 4. sandy loam A horizon of the White Store series

expressed as percentage of volume of saturated soil or of the cylinder, is given in column 3 of table 1.

The saturated soil remaining in the cylinders, after the excess from swelling

had been removed, was dried at 105°C. and the volume-weight ratio determined on the basis of volume of the cylinders, which was 600 cc. These values are given in column 2 of the table. After the soils were oven-dried, shrinkage was measured with number 40 motor oil, and expressed as percentage of the volume of the cylinders. This measurement of shrinkage was obtained by placing a lid on the bottom end of the cylinder and weighing the amount of heavy oil necessary just to fill the voids caused by shrinkage. The weight values of oil were transformed to a volume basis in the calculation of shrinkage in column 4. Moisture-equivalent determinations were made in the usual manner, with the exception that 32 cc. of 2-mm. soil was used in each cup, saturated in water for 24 hours, and then centrifuged for 40 minutes at 1000 g. After centrifugation the surface half of each sample was discarded and the lower half used for determination of moisture content or moisture equivalent. The latter procedure is a necessary modification of the usual method because in the White Store and Orange soils a marked moisture gradient occurs from top to bottom of the cups after centrifugation, or along the line of the centrifugal radius. Sometimes free water is found on the surface after centrifugation. To determine the xylene equivalent, the soil samples were oven-dried in the cups and then saturated with xylene for 30 minutes, centrifuged, and weighed. The difference between the xylene equivalent and the moisture equivalent, which might be called "imbibitional water value," affords an approximation of the characteristics of a soil which are manifested by volume changes on wetting and drying (column 5 of table 1).

Inspection of the data in table 1 and of the oven-dry soil cores in figure 1 should reveal the magnitude of volume changes and the interrelation of the measurements. In figure 1 the samples numbered "4" are from a sandy loam A horizon that does not exhibit appreciable shrinkage.

The author has found the difference between the moisture equivalent and the xylene equivalent to be a useful measure of physical properties of fine-textured Piedmont B horizons which markedly affect tree growth. With due consideration given to other factors, soils with large differences between moisture equivalents and xylene equivalents are poor forest sites and those with small differences are good forest sites.
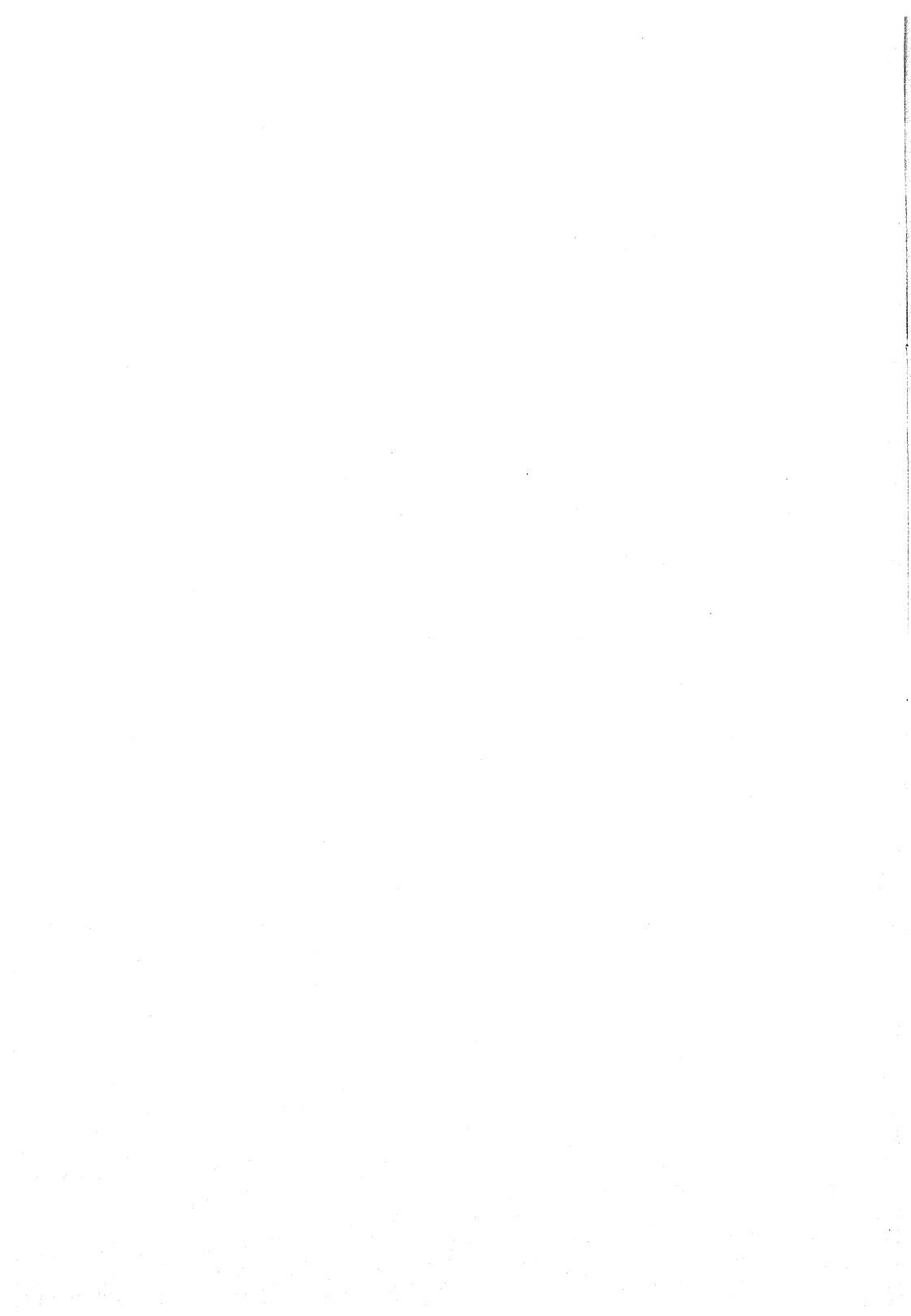
NITROGEN FIXATION BY AZOTOBACTER IN ASSOCIATION WITH OTHER BACTERIA

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The literature on *Azotobacter* (4–11) contains numerous references to experiments in which nitrogen fixation has been stimulated through the presence of associated organisms. When the origin of the benefit in such experiments is not clear, it usually has been ascribed somewhat indefinitely to a "symbiosis." A survey of these trials reveals that in nearly every case fixation by the pure culture of azotobacter has been very poor in comparison with that obtained in more recent investigations, suggesting that the medium or technique employed was unsatisfactory for best development of the organism. The role of associated microorganisms may then often be simply an alteration of the medium so that it becomes more suitable for growth of the azotobacter. Support for this view is provided by observations made by us recently in connection with our studies on the mechanism of biological nitrogen fixation.

EXPERIMENTAL

In this research we routinely carry working cultures of *Azotobacter vinelandii* by transferring daily 1 ml. of a 24-hour culture into 15 ml. of liquid medium containing Burk's (1) salts plus 2 per cent sucrose and 0.25 per cent agar. Iron is supplied as the humate (3). The medium is contained in a 6-ounce prescription bottle, which is incubated at 30°C. on its side to increase the surface exposed. Under these conditions 15 to 25 mgm. N_2 is fixed in 24 hours. Extreme care is taken to avoid contamination, a factor which has not been considered adequately in many experiments with *Azotobacter* (12). The culture is routinely tested for purity by microscopic examination (gram stain) and by subculture into peptone broth (2, 13). In spite of all precautions, occasionally a culture becomes contaminated. When this occurs, the culture is discarded, and a new series of transfers is started from the stock agar culture kept at 4°C.

Usually when a contaminant appears, the proportion of the foreign organism in the population is small initially, but on continued transfer, it increases at the expense of the *Azotobacter* with a resultant decrease in fixation. Occasionally, however, we have observed that the contaminated culture is superior to a pure culture in fixation of nitrogen. Recently we picked up a contaminant which stimulated fixation but which did not increase its relative numbers when the mixed culture was transferred.[1] We maintained this impure culture for

[1] We have transferred this mixed culture more than 30 times during a 4-month period without change in relative numbers of each species or in nitrogen-fixing ability. Counts by the Petroff-Hausser chamber method indicated that the contaminant comprised about 5 per cent of the total population. An interesting effect of the association was that the green pigment characteristic of the *vinelandii* species disappeared.

several weeks, periodically estimating its nitrogen-fixing ability in comparison with our pure stock culture. Typical results from a number of experiments harvested at 12 to 48 hours are shown in table 1.

To determine whether the increased fixation arose from activity of the foreign organism or merely from a superior strain of azotobacter in the mixture, pure cultures of both the azotobacter and the contaminant were isolated from the mixed culture. The contaminant was unable to fix nitrogen and was accordingly kept on nutrient agar slants. Whenever it was required for mixing with a pure culture, several loops of its growth were transferred to 15 ml. of

TABLE 1

Nitrogen fixation by pure and mixed cultures of Azotobacter

EXPERIMENT NUMBER	HOURS	NITROGEN FIXED*	
		Pure stock culture	Mixed culture
1	15	5.7	18.2
		7.9	18.1
2	25	22.4	45.1
		22.7	35.4
3	47	31.2	40.4
		33.8	48.4
4	12	5.6	13.6
		5.6	10.1
5	23	10.2	33.5
		14.5	39.0
6	48	26.7	37.0
		26.1	41.0

* Values in mgm. N/100 ml.; this includes nitrogen in inoculum, which was 1 ml. in 15 ml. The heavy inoculum of active growing cells explains the excellent fixation observed, which in some instances was more than 20 mgm. in 12 hours.

the nitrogen-free medium and allowed to incubate for several hours, then 1 ml. was added to the bottle freshly inoculated with the pure culture of *Azotobacter vinelandii*. Results in table 2 show that the increased nitrogen fixation in the mixed culture was largely due to "symbiosis," since pure strains isolated from this were little, if any, better than our original stock from which they were derived. If the pure strains of *A. vinelandii* and the contaminant were mixed and transferred daily for a few times, the results were the same as those obtained with the original mixed culture.

A bacteriological examination[2] of the organism showed that it was a spore-forming gram-positive rod, which was tentatively but not absolutely identified

[2] We thank Jack Voss and Elizabeth McCoy for this preliminary examination.

as *Bacillus circulans*. Strains of other bacilli as well as various other species in the Wisconsin collection were tested for ability to stimulate nitrogen fixation by *A. vinelandii*, including: *B. subtilis* (Marburg), *B. mesentericus*, *B. truffauti*, *Escherichia coli*, *Achromobacter radiobacter*, *Saccharomyces cerevisiae*, *Clostridium pasteurianum*, and a number of species of the rhizobia. All except *C. pasteurianum* were unable to increase the quantity of nitrogen fixed by the strains of *A. vinelandii*. The results with *C. pasteurianum* are given in table 2

TABLE 2

Nitrogen fixation by strains of Azotobacter with and without a contaminant

EXPERIMENT NUMBER	HOURS	STRAIN NUMBER*	NITROGEN FIXED†	
			Pure culture	Plus contaminant
Azotobacter and bacillus from mixed culture				
7	21	1	6.9	11.1
		2	9.5	16.2
		3	8.2	16.2
8	12	1	7.0	19.8
		2	6.7	27.2
		3	8.3	26.4
9	12	1	5.0	20.1
		2	8.9	22.3
		3	7.3	21.7
10	41	1	16.5	31.4
		2	20.0	32.5
		3	18.9	32.5
11	12	2	10.8	18.8
		3	10.4	26.7
Azotobacter and Clostridium pasteurianum				
12	12	2	6.7	19.5
13	12	3	8.9	21.0

* Strain 1 was *Azotobacter* stock culture; strains 2 and 3 were pure cultures of *Azotobacter* isolated from mixed culture.

† Values in mgm. N/100 ml.; this includes nitrogen in inoculum, which was 1 ml. in 15 ml.

(experiments 12 and 13). With this organism, the interpretation is somewhat complicated by the fact that it also fixes nitrogen. In the short incubation time used, however, the fixation by *C. pasteurianum* alone was less than 1 mgm. even when favored by anaerobic conditions. Microscopic examination of the mixed culture indicated that the increase in fixation was due to stimulation of growth of the azotobacter.

To learn whether the stimulation of the azotobacter arose from a hitherto

unrecognized heat-stable growth factor required by this organism and synthesized by the contaminant, autoclaved suspensions of the latter as well as heated cultures were furnished pure cultures of the azotobacter without result. A second possibility was that the organism converted the carbohydrate into a more readily utilizable source of carbon such as ethyl alcohol or acetate. Experiments were begun to test this hypothesis, but difficulty was experienced in keeping the alcohol and the salts of the lower fatty acids supplied at the proper level and in initiating growth. While these trials were in progress, the origin of most of the stimulation was somewhat accidentally uncovered when a

TABLE 3

Effect of source of iron on nitrogen fixation by pure and mixed cultures of Azotobacter

EXPERIMENT NUMBER	SOURCE OF IRON	HOURS	STRAIN NUMBER	NITROGEN FIXED*	
				Pure culture	Plus contaminant
14	New humate	8	2	1.9	1.6
		17		10.3	9.8
		23		18.4	23.8
15	Old humate	16	3	5.9	11.0
	New humate	16		13.1	16.4
16	Old humate (single)	18	2	6.5	13.4
					13.2
	Old humate (double)			10.3	14.1
				10.4	13.7
17	Old humate	23	1	10.5	25.8
				9.8	25.3
	Old humate + Fe			26.6	27.8
				27.2	26.7

* Values in mgm. N/100 ml.; this includes nitrogen in inoculum, which was 1 ml. in 15 ml.

new solution of iron humate was prepared. In the previous experiments a preparation had been used which had given satisfactory results for several months even though part of the iron had precipitated. Before it was exhausted a new supply was made, and when this was used in an experiment, the stimulating effect of the contaminant disappeared. The cause of this is evident from the data in table 3. In the presence of the new humate, nitrogen fixation by the pure culture was markedly superior to that obtained with the old preparation. The apparent stimulation by the contaminant in the presence of the new humate scarcely exceeds the difference frequently observed with duplicates.

These results suggested that the old humate preparation had become deficient in some essential constituent, probably *available* iron. Analysis of the

preparations showed that the new humate contained 2.5 mgm. Fe/ml. in comparison with less than 0.5 mgm. Fe/ml. in the old preparation. Nor is it certain that all this iron was available after autoclaving with the salts in the medium. We concluded, then, that the function of the contaminant had been to make available certain minerals, especially iron, which were present in unusable forms and which consequently made the medium deficient for maximum fixation. It should be noted, however, that fixation by the pure culture with the old humate was not inconsiderable and definitely higher than that usually reported for such experiments. For this reason a deficient medium was not suspected until the new preparation demonstrated that the rate and extent of fixation could be materially increased.

If the suggested explanation was true, then additional old humate should reduce the stimulation noted, and fortification with iron should make it equivalent to the new preparation. Both of these predictions proved to be true. If 2 ml. of the old humate preparation was used instead of the usual 1 ml. per liter, greater fixation was obtained in the pure culture, and the stimulation was not so marked. Also if the humic acid was precipitated with acid, 10 per cent Fe added as ferrous sulfate (based on dry weight of humic acid), and the precipitate redissolved with alkali, the resulting preparation behaved as did the new humate. (See table 3, experiments 16 and 17.)

DISCUSSION

The results of these experiments have a wider implication for studies on nitrogen fixation, especially by *Azotobacter*, than the mere solution of the problem that led to this research. The literature on *Azotobacter* is filled with accounts of stimulating nitrogen fixation by various means, including associated organisms, addition of different materials to the medium, and alteration of experimental technique. A study of these experiments reveals that almost without exception the fixation by the pure culture was rather poor—values of 1 to 5 mgm./100 ml. in 3 to 14 days. Since in the modern studies under optimum conditions with reference to carbon source, supply of minerals, and aeration, fixation of 15 to 25 mgm. N/100 ml. in 24 to 36 hours is not uncommon, the suspicion arises that the reported stimulation of the various agents is due simply to alteration of a deficient medium or experimental method. Indeed, the rate of fixation in many of these studies is so slight that the significant finding is, not that the particular change in experimental conditions stimulated fixation, but that any possible change would have done otherwise.

In this connection the role of the undetected contaminant should not be overlooked. This factor has been neglected in many investigations because of the comforting but erroneous belief that use of a nitrogen-free medium assures freedom from foreign visitors. Winogradsky (12) has disposed of this myth so effectively that critical deductions regarding the physiology of the organism are possible from experiments (past or future) only when unequivocal evidence of purity of culture is provided. The contaminant may affect the results in a variety of ways: by decreasing fixation, by stimulating fixation (making avail-

able necessary minerals or decreasing the level of inorganic nitrogen), or by providing a more desirable source of carbon for growth and respiration of the azotobacter. In our own studies this last point could not be critically determined, since in long-time experiments secondary effects arise which complicate interpretation of the results. These effects include changes in the concentration of the substrate and alteration in the pH. It appears probable that the metabolism of the associated organism may provide a much more delicate mechanism for control of this factor (carbon source) than the efforts of the experimenter, and thus it may play a role in the beneficial results. Another possibility is that, although *Azotobacter* alone cannot effectively use organic sources of nitrogen, liberation of ammonia from these by a contaminant in a medium, such as soil, which contains "unavailable" nitrogen would stimulate the development of the nitrogen-fixing organism.

The significance of these results for soil microbiology should be mentioned. Conditions are probably seldom optimum in the soil for nitrogen fixation by the azotobacter; therefore, the unusually high rates of fixation obtained in the laboratory are rarely, if ever, duplicated in nature. Associated microorganisms may stimulate the normal, slow rate of fixation by liberating from soil minerals essential elements, especially Fe and Mo; by providing superior sources of carbon, such as alcohols and lower fatty acids; or by assimilating free ammonium ions. In return, the azotobacter provides an excellent source of growth factors including biotin, riboflavin, nicotinic acid, and pantothenic acid[3] as well as a supply of nitrogen (2). Such a process is called "symbiosis"; in using the term, however, it should be kept in mind that no mysterious, ill-defined effects are implied, only straightforward well-recognized physiological reactions.

SUMMARY

An aerobic sporeformer isolated as a contaminant from a culture of *Azotobacter vinelandii* markedly stimulated nitrogen fixation by this organism. The two species could be continuously grown together without the contaminant's dominating the population and consequently reducing the nitrogen fixed. The same results were obtained by mixing pure cultures of the contaminant with strains of *Azotobacter* at the beginning of an experiment. Attempts to replace this contaminant by other aerobic sporeformers, by rhizobia, and by other nonsporeformers were unsuccessful.

Stimulation of nitrogen fixation was obtained with a mixed culture of *Azotobacter vinelandii* and *Clostridium pasteuranium* under conditions in which appreciable nitrogen fixation by the latter would not be expected.

The stimulative effect of the contaminant was shown to depend on the use of a medium in which the readily available iron was not optimum because of an unsatisfactory preparation of iron humate. Under these conditions fixation by the *Azotobacter*, although good and decidedly higher than most values found in the literature, was not maximum. When a new preparation of humate was

[3] Lee, S. B. Unpublished results, 1942.

used or additional iron was supplied the old preparation, the stimulation was no longer evident.

The implications of the results for reports in the literature which deal with beneficial effects of various treatments on nitrogen fixation by *Azotobacter* are discussed.

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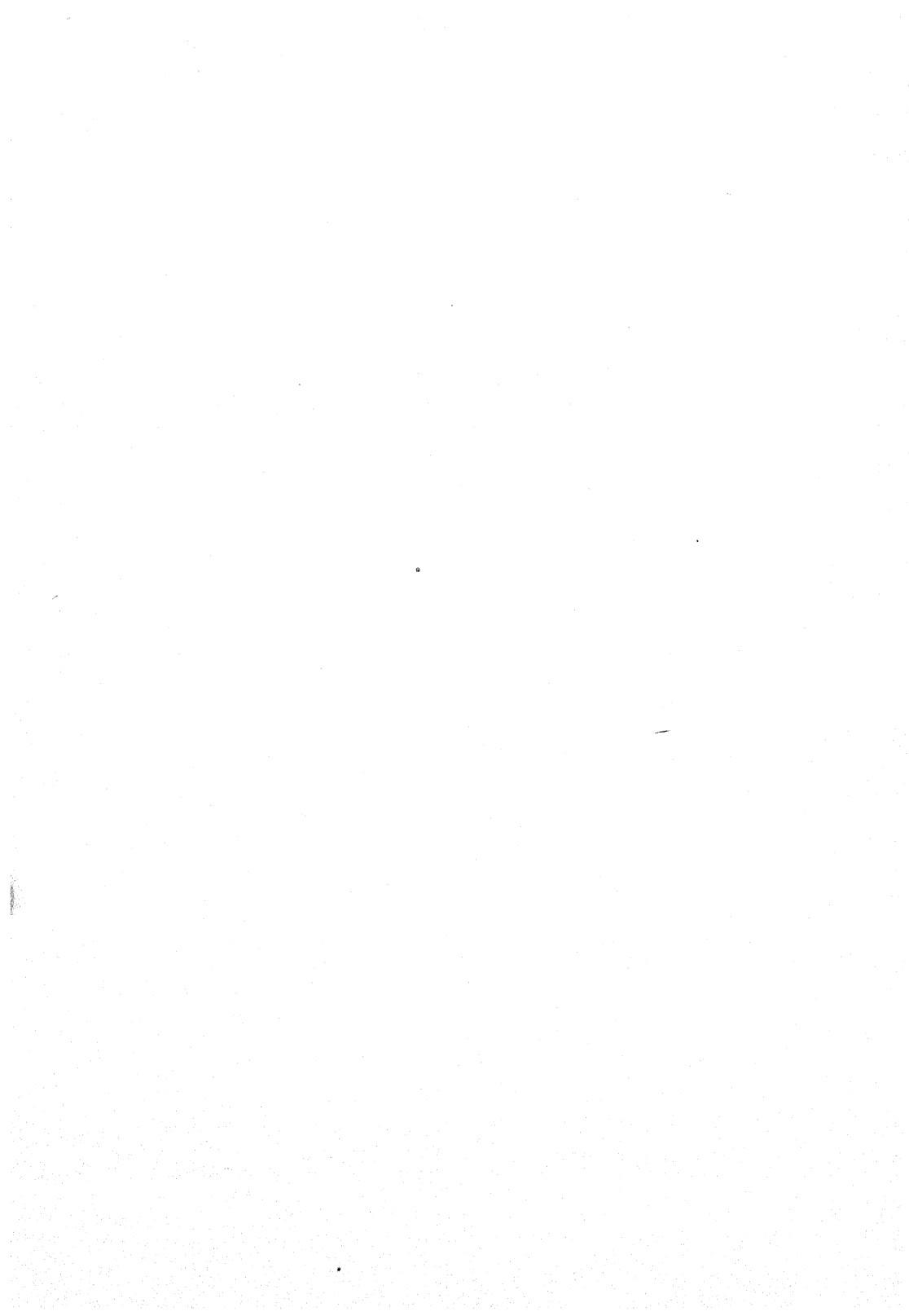
INFLUENCE OF POTASSIUM CHLORIDE ON NITRIFICATION IN BEDFORD SILT LOAM[1]

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The influence of potassium chloride on nitrification has been studied by Greaves, Carter, and Goldthorpe (4), Smith (8), Protasov (7), Vandecaveye (10), Mack and Haley (6), and many others. Generalization is impossible, since this influence appears to depend on the conditions under which experiments are conducted. It is known that under certain conditions potassium chloride may appreciably inhibit nitrification, but very few of these conditions have been identified. Protasov (7) has reported that potassium chloride favors the loss of nitric nitrogen from well-drained soils but increases nitric nitrogen in poorly drained soils.

The junior authors have noted that relatively high concentrations of potassium chloride consistently decrease nitrification rates as determined in the laboratory on several soil types of common occurrence in Indiana. In view of the importance of nitrification to successful plant growth, and the common use of potassium chloride as a fertilizer, an effort has been made to determine how potassium chloride inhibits nitrification.

MATERIALS AND METHODS

All the experiments reported here were conducted in the laboratory. Continuously cropped Bedford silt loam from the Purdue University Moses Fell Annex farm at Bedford, Indiana, was used throughout this investigation. This soil had received no lime or fertilizer in the last 20 years. Soil was brought into the laboratory and sieved through a 10-mesh screen, after which it was stored in a covered container at a moisture content between 10 and 16 per cent of its water-holding capacity. The water-holding capacity was approximately 45 per cent of the weight of the soil. The stock soil was mixed thoroughly several times during the investigation. Physical and chemical analyses of Bedford silt loam are given by Tharp, Bushnell, and Adams (9).

In setting up the various experiments, moist soil equivalent to 50 gm. of oven-dry soil was weighed into 9-ounce glass tumblers. The soil was limed with 2,000 p.p.m. of $CaCO_3$ and then treated as desired with C.P. grade salts, after which the moisture content was established at either 50 or 66 per cent of moisture-holding capacity. The tumblers of soil were incubated in 87 to 97 per cent relative humidity at a temperature between 28 and 31°C. Unless otherwise indicated, each tumbler was analyzed for nitric nitrogen after 30 days of incuba-

tion.   The water content of the soil was restored to the original level at 7-day intervals during the incubation period.

Nitric nitrogen usually was determined by the phenol-disulfonic acid method, essentially as modified by Fraps and Sterges (3).   The K.W.S.Z. photometer, described by Withrow, Shrewsbury, and Kraybill (12), was used to compare the intensity of color developed.   The machine was checked periodically to test the relative strength of the photoelectric cells.   During the entire investigation a maximum of only 0.1 per cent variation in light transmission was observed in color standards.   This variation is considered insignificant.   A number two, blue filter was used in the machine.   Transmission of light was determined with the K.W.S.Z. photometer for known concentrations of nitric nitrogen in 20- and 10-mm. absorption cells.   Transmission-concentration curves were then plotted for each cell.   The transmission measurements of the photometer were found to be very satisfactory for determining nitric nitrogen in soil leachates.

Since chlorides are known to influence the phenol-disulfonic acid method of nitrate determination, precautions were taken to remove chlorides from soil leachates where this was necessary.   When the nitric nitrogen content of soils was high, 1-cc. aliquots of leachate were sufficient for developing a suitable color.   The removal of chloride by precipitation with silver sulfate was found to be unnecessary when such small aliquots of leachate were used.   The recovery of added nitrate by the technique described, whether accomplished immediately after addition or after 1 month of incubation, was not influenced by concentration of potassium chloride.   About 88 per cent of added nitrate was recoverable immediately after addition.   This recovery was consistent in several trials.

RESULTS

Influence of varying concentrations of potassium chloride on accumulation of nitrates

Stock soil was limed with 2000 p.p.m. of $CaCO_3$ and then variously treated to produce KCl concentrations of 0, 95, 190, 380, and 760 p.p.m.   The water content of the soil was adjusted to 66 per cent of the moisture-holding capacity. Analyses for nitric nitrogen were made at the beginning and at the end of 30 days' incubation.   The accumulated nitrate was determined on soil samples to which no $(NH_4)_2 SO_4$ had been added and on samples to which 2820 p.p.m. of $(NH_4)_2$-SO_4 had been added.   The results are shown in table 1.

Inhibition of nitrification of the added $(NH_4)_2SO_4$ is noted at concentrations of KCl above 380 p.p.m.   The critical concentration must be presumed to occur between 190 and 380 p.p.m., under the conditions of our experiment, though it might differ somewhat on soil of another moisture content.

There is no significant influence of KCl on nitrification of soil nitrogen.   On several occasions slight inhibition of such nitrification has been observed, but these differences usually have not been sufficiently large to be statistically significant at the 5 per cent level.   It seems probable that under ideal conditions for nitrification, ammonia may rapidly become the limiting factor in nitrification of soil nitrogen, thus tending to minimize the effect of KCl.

Influence of potassium chloride on progressive transformation of ammonia to nitrate

Soil was limed with 2000 p.p.m. of $CaCO_3$ and divided into two equal parts, one of which was mixed with 600 p.p.m. of nitrogen as $(NH_4)_2 SO_4$. Each of these parts was again subdivided into two parts, one each of which received 760 p.p.m. of KCl. Tumblers were prepared in the usual way and incubated. After 5, 10, 15, 20, and 30 days' incubation five replicate tumblers of each treatment were removed and each was analyzed separately for ammonical, nitrous, and nitric nitrogen. As the samples were removed from the incubator, the soils were leached with 4 per cent KCl solution, and this leachate was then used for the various determinations. An aliquot of the leachate was taken for nitrite determination by the α-napthalamine-sulfanilic acid method (3). The remainder of the leachate was made slightly alkaline with NaOH, and the ammonia was distilled into standardized acid. Nitrites and nitrates in the leachate

TABLE 1

Influence of concentration of potassium chloride on nitrate accumulation in Bedford silt loam after 30 days' incubation

AMMONIUM SULFATE ADDED	NITRIC NITROGEN PRODUCED IN SOIL TREATED AS INDICATED*					SIGNIFICANT DIFFERENCE† (5 PER CENT LEVEL)
	p.p.m. of KCl added					
	0	95	190	380	760	
p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	
0	45	44	46	42	46	
2820	264	247	253	222	214	16

* Moisture was maintained at 66 per cent of the moisture-holding capacity of the soil. The soil received a basic treatment of 2,000 p.p.m. of $CaCO_3$.

† Based on six replications.

were then reduced with Devarda alloy, and the ammonia was again distilled into standardized acid.

The results, summarized in table 2, show that a concentration of 760 p.p.m. of KCl does not cause nitrites to accumulate but does cause a greater amount of ammonia to remain unchanged in the soil. This suggests that nitrite formation is inhibited. There is no conclusive evidence in table 2 that nitrate formation is unaffected. Other results, however, suggest that nitrate formation is not appreciably retarded by KCl. At each of five 5-day intervals during 30 days' incubation, 51 p.p.m. of nitrous nitrogen as $NaNO_2$ was added to soil variously treated with KCl. On the thirtieth day the soils were analyzed for nitric nitrogen. As shown by the following results, based on three replications, there is no evidence that KCl appreciably inhibited the accumulation of nitrates: soil receiving no KCl produced 269 p.p.m. nitric nitrogen; 95 p.p.m. KCl, 223 p.p.m. NO_3; 190 p.p.m. KCl, 243 p.p.m. NO_3; 380 p.p.m. KCl, 215 p.p.m. NO_3; 760 p.p.m. KCl, 225 p.p.m. NO_3; significant difference (5 per cent level), 89 p.p.m.

Analyses for numbers of *Nitrosomonas* sp. and *Nitrobacter* sp. (table 3) tend to

confirm this conclusion. Numbers of *Nitrosomonas* may be slightly increased by 190 p.p.m. of KCl but slightly reduced by 760 p.p.m. Numbers of *Nitrobacter* are not reduced by additions of KCl and may be slightly increased. The differences in table 3 are not statistically significant in all cases, but when

TABLE 2

Influence of potassium chloride on progressive transformation of ammonia to nitrate in Bedford silt loam during 30 days' incubation

INCUBATION PERIOD	KCl ADDED	NITROGEN RECOVERED IN SOIL RECEIVING							
		No (NH₄)₂SO₄				600 p.p.m. of N as (NH₄)₂SO₄			
		N recovered as			Total	N recovered as			Total
		NH₄	NO₂	NO₃		NH₄	NO₂	NO₃	
days	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
0	0	16	0.03	26	42	605	0.03	26	631
	760	16	0.03	26	42	605	0.03	26	631
5	0	20	0.22	29	49	578	1.12	32	611
	760	20	0.44	30	50	584	0.86	29	614
10	0	12	7.6	48	68	527	13	50	590
	760	15	5.2	42	62	556	10	43	609
15	0	8	6	69	83	497	5	84	586
	760	7	7	67	81	530	8	62	600
20	0	8	0	74	82	445	0	139	584
	760	6	0	70	76	506	0	82	588
30	0	3	0	80	83	259	0	319	578
	760	3	0	76	79	372	0	174	546

TABLE 3

Influence of potassium chloride on numbers of Nitrobacter and Nitrosomonas in Bedford silt loam after 30 days' incubation

KCl ADDED	NUMBERS OF NITROSOMONAS	NUMBERS OF NITROBACTER
p.p.m.		
0	67,000	5
190	90,000	12
760	31,000	26
Significant difference (5 per cent level).................	70,000	21

interpreted with other evidence in mind seem to confirm the conclusion that *Nitrosomonas*, but not *Nitrobacter*, is inhibited by KCl. Numbers of nitrifiers were determined by the dilution technique, as refined by Halvorson and Ziegler (5).

Other experiments, the results of which are not reported here, have shown that the effect of KCl on nitrite formation persists after 60 days, the longest incubation period tested.

Analysis of the influence of chloride and potassium ions on nitrification

It is pertinent to a proper understanding of the action of KCl on nitrification to know whether the inhibition of nitrification is due to the potassium ion, the chloride ion, the KCl molecule, or a combination of these factors.

Soil was limed and $(NH_4)_2SO_4$ added in the usual manner. Soil aliquots were then treated with mixtures of KCl and $CaCl_2$. The chloride ion being held constant at 45 p.p.m., the ratio of KCl to $CaCl_2$ was varied in six steps from 5 parts KCl: 0 $CaCl_2$, to 0 KCl: 5 parts $CaCl_2$. The level of chloride was then raised to 90 p.p.m., and the ratios were varied as before. Finally chloride concentrations of 180 and 360 p.p.m. were established, and the ratios were again varied in six steps. The same experiments were made with mixtures of KCl and NaCl.

The treated soils were incubated 30 days at 50 per cent of the moisture-holding capacity and then analyzed for nitric nitrogen. Means of three replications are given in table 4.

In analyzing the results it must be kept in mind that though the data in table 4 are classified in only two ways, namely, ratios of KCl to $CaCl_2$ (or NaCl), and concentration of chlorides, each way of classification involves several variables. The decreasing amounts of accumulated nitrates shown in horizontal rows may be due to increasing KCl, increasing chloride ions, increasing potassium ions, increasing calcium (or sodium) ions, or increasing $CaCl_2$ (or NaCl). The decreasing amounts of accumulated nitrates shown in vertical columns may be due to decreasing KCl, increasing $CaCl_2$ (or NaCl), decreasing potassium ions, or increasing calcium (or sodium) ions.

In that part of table 4 involving $CaCl_2$, the accumulation of nitrates decreases in response to some factor or factors influencing the horizontal row of figures. Also, the accumulation of nitrates decreases in response to factors influencing the vertical columns. These facts eliminate the potassium ion and the KCl molecule as possible sources of variation, since these two factors cannot both inhibit and stimulate nitrification simultaneously. Hence, variation in the vertical columns must be due to either calcium ions or the $CaCl_2$ molecule. Variation in the horizontal rows may be due to the chloride ions, the calcium ions, or the $CaCl_2$ molecule. Since variation in horizontal rows is much greater than in vertical columns and since variation does occur in that horizontal row where all chloride is supplied as KCl we may assume that chloride ions are exerting a depressing effect on nitrification.

Where KCl: NaCl ratios were used the results may be interpreted with more certainty. Since there is no significant variation within vertical columns, KCl, NaCl, potassium ions, and sodium ions may be eliminated as sources of variation. Thus the variation within horizontal rows must be due to the chloride ions.

A second experiment similar in design to that just described was set up but

was replicated only twice. In this experiment potassium ions were held constant while chloride ions were varied by treating soil with mixtures of KCl and K_2CO_3 and of KCl and K_2SO_4. Potassium was held constant at concentrations of 50, 100, 200, and 400 p.p.m., while chloride concentration was varied at each level. The results are given in table 5.

We may reason as before, that the decreasing rate of nitrate accumulation shown in horizontal rows may be due to increasing potassium ions, increasing

TABLE 4

Influence of chloride ions on nitrification in Bedford silt loam after 30 days' incubation

RATIO OF CHLORIDE IONS SUPPLIED BY	NITROGEN NITRIFIED* IN SOILS TREATED WITH MIXTURE OF CHLORIDES IN TOTAL CONCENTRATIONS INDICATED				MEANS†
	p.p.m. Cl ion added				
	45	90	180	360	
	p.p.m.	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
KCl:CaCl₂					
5:0	108	110	106	63	96
4:1	104	105	93	59	90
3:2	115	102	92	51	90
2:3	110	110	89	48	89
1:4	97	91	75	46	77
0:5	103	96	58	46	76
Means‡........	106	102	86	52	
KCl:NaCl					
5:0	179	170	172	118	160
4:1	176	155	157	126	153
3:2	155	173	159	122	160
2:3	180	176	163	126	162
1:4	169	158	160	126	153
0:5	179	178	156	105	154
Means‖......	178	168	161	120	

* Mean of three replicates.

† Significant difference between means for KCl:CaCl₂ = 10 p.p.m. of nitrogen; for KCl:NaCl, 40 p.p.m. of nitrogen.

‡ Significant difference = 8 p.p.m. of nitrogen.

‖ Significant difference = 32 p.p.m. of nitrogen.

chloride ions, increasing carbonate (or sulfate) ions, increasing KCl, or increasing K_2CO_3 (or K_2SO_4). The decreasing rate of nitrate accumulation shown in vertical columns may be due to increasing KCl, increasing chloride ions, decreasing K_2CO_3 (or K_2SO_4), or to decreasing carbonate ions (or sulfate ions). Since K_2CO_3 and carbonate ions could not increase and at the same time decrease nitrification, these two factors must be eliminated as possible causes of variation. The same is true of K_2SO_4 and sulfate ions. Decreasing nitrate accumulation in horizontal rows must be due to increasing concentrations of potassium ions, chloride ions,

or KCl. Decreasing nitrate accumulation in the vertical columns must be due to increasing concentration of chloride ions or to increasing concentration of the KCl molecule. Thus potassium ions are not responsible for variation within vertical columns. There is some evidence that potassium ions have no part in producing variation within horizontal rows. For example, where potassium is supplied entirely as KCl, increasing concentrations apparently cause a decreasing accumulation of nitrates, but where potassium is supplied as K_2CO_3 or

TABLE 5

Influence of potassium ions on nitrification in Bedford silt loam after 30 days' incubation

RATIO OF POTASSIUM IONS SUPPLIED BY	NITROGEN NITRIFIED* IN SOILS TREATED WITH MIXTURE OF POTASSIC SALTS IN TOTAL CONCENTRATIONS INDICATED				MEANS†
	p.p.m. K ion added				
	50	100	200	400	
KCl:K₂CO₃					
5:0	128	141	119	92	120
4:1	146	129	128	95	124
3:2	130	128	130	111	122
2:3	139	136	130	122	132
1:4	134	124	144	138	135
0:5	142	129	141	129	135
Means‡......	137	131	132	114	
KCl:K₂SO₄					
5:0	108	144	130	90	118
4:1	137	141	118	87	121
3:2	128	134	119	103	121
2:3	134	145	137	106	130
1:4	148	124	143	102	132
0:5	145	128	135	144	138
Means‖	133	136	130	107	

* Mean of two replications.
† Significant difference between means for KCl:K₂CO₃ = 12 p.p.m. of nitrogen; for KCl: K₂SO₄, 40 p.p.m. of nitrogen.
‡ Significant difference = 10 p.p.m. of nitrogen.
‖ Significant difference = 33 p.p.m. of nitrogen.

K_2SO_4, increasing concentrations have little or no influence on the accumulation of nitrates.

It seems probable from these experiments that the cause of inhibition of nitrification in the presence of high amounts of KCl is primarily chloride-ion concentration. This is interesting in view of the fact that many synthetic media in which nitrite formation occurs contain much higher concentrations of chloride ion than have been added to soil in these experiments. It must be presumed that if the chloride ion influences nitrite formation it does so indirectly by some action on soil.

Investigation of some means by which potassium chloride may inhibit nitrification

According to Smith (8), KCl depressed nitrification in several soil types studied but lime overcame this effect in part.   Smith infers that the lime may aid nitrification by neutralizing acid produced by the reaction of KCl with soil colloids. In our experiments, KCl did not significantly increase H-ion concentration during one month of incubation.   The pH of the soil was lowered during incubation, presumably by the formation of the nitrate ion and the release of sulfate from added ammonium sulfate, both of which form strong acids with hydrogen replaced from soil colloids.

It has been observed that 760 p.p.m. of KCl reduced the amount of CO_2 evolved from 100 gm. of soil during 30 days' incubation from 17 mgm. to 14.5 mgm.   Although low concentrations of CO_2 are known to retard nitrification (2, 11), it seems unlikely that a decrease of this proportion could be the entire explanation of the action of KCl on nitrification.

It has not been possible to overcome the harmful effect of KCl on nitrification by additions of varying concentrations of $MgSO_4$, $CaCO_3$, or H_3PO_4.   This fact suggests that nitrification in KCl-treated soil is not retarded by unbalanced ionic relationships.

DISCUSSION

The authors feel that many apparent discrepancies in the literature may be due to failure of various workers to conduct their experiments with soils of equivalent water contents.   Undoubtedly there are other factors upon which the action of chloride on nitrification depends.   It would seem that the soil colloid technique of Albrecht and McCalla (1) might be useful in further studies.

Since the chloride-ion concentration necessary to inhibit nitrification in Bedford silt loam is rarely obtained under farming conditions, the inhibition of nitrification in soil by chlorides probably is of practical importance only in laboratory studies.

SUMMARY

The critical concentration of KCl for measurable inhibition of nitrification in Bedford silt loam at 66 per cent of water-holding capacity was found, in laboratory experiments, to occur between 190 and 380 p.p.m.   Nitrite formation, but not nitrate formation was inhibited by KCl.   The chloride ion was found to be responsible for inhibition of nitrification.

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WATER-PERMEABLE JACKETED THERMAL RADIATORS AS INDICATORS OF FIELD CAPACITY AND PERMANENT WILTING PERCENTAGE IN SOILS

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Recent publications (3, 4) by Shaw and Baver have outlined a method by which soil moisture may be interpreted as a function of the heat conductivity of soils. The readings obtained by this method are the measurement of unbalance in a Wheatstone bridge resulting from the application of a heating current to a coil buried in the soil under investigation. This heater element in the soil forms one leg of the bridge, and the conductivity of the soil, which is affected by its moisture content (2), controls the liberation of heat from the element. The initial Shaw-Baver circuit is shown in figure 1. From this circuit it may be seen that unbalance in the bridge is the result of the difference in radiation from two identical heater elements, one in dry soil and the other in moist soil. The variable resistor in the bridge then registers the amount of unbalance thus caused in any time by the change made necessary in that resistance to keep the bridge in balance. The second circuit supplied by Shaw and Baver has a milliammeter in place of the galvanometer in the bridge and substitutes a fixed resistance for the dry-soil heater element. Here the unbalance in the bridge for any time is read directly on the milliammeter and no adjustment is made during the run except to keep the current flow steady.

The curves that result from plotting data obtained by the use of either of the Shaw-Baver circuits are affected, as was the intention, by the heat conductivity of the soil in which the heater elements are buried. Patten (2) has shown that each soil has its own heat-conductivity characteristics. The result is that each soil in use must be calibrated with this electrical equipment before the instrument can be applied in the field, an unfortunate handicap in an area where extensive plantings of even a single crop are distributed over a broad range of soil types.

Work with Bouyoucos' plaster electrical conductors (1) suggested that if the heater element in the soil were given a covering of porous material that would have its own moisture-holding characteristics, this jacket would absorb the heat emanating from the heater coil, making the resulting readings a function of the moisture content of the jacket and eliminating the contact difficulties between soil and elements that arise when nonjacketed heaters are used. It has to be assumed that such a jacket can adjust itself to soil-moisture changes. Plaster of paris, a porous medium that lends itself to the making of such jackets,

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was cast, therefore, as a concentric jacket one-eighth inch thick about the 15-mm. glass tubes upon which the heater wires had been wrapped (fig. 2).

To determine whether such heater elements placed in two soils of markedly different types would show comparable readings at field capacity and again at the permanent wilting percentage in each soil, heater elements were buried in
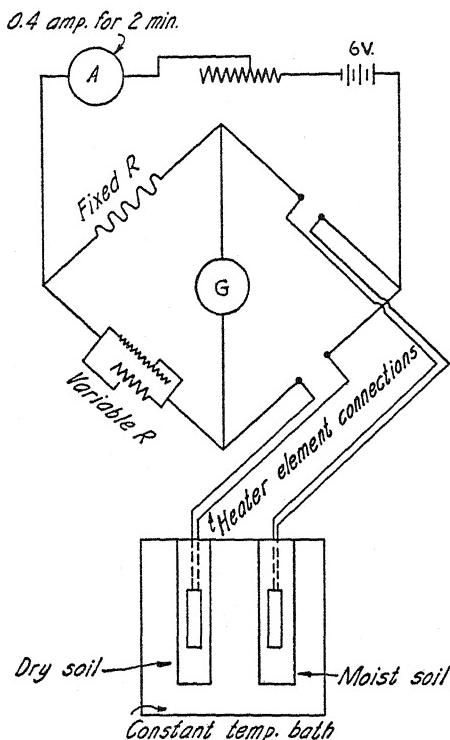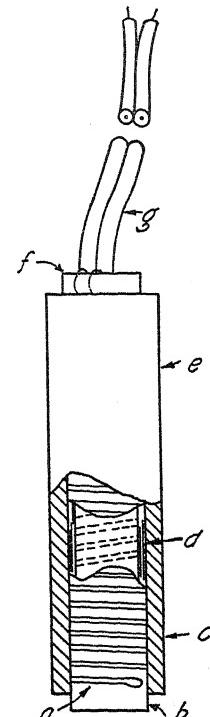
FIG. 1. ORIGINAL CIRCUIT USED BY SHAW-BAVER TO MEASURE HEAT CONDUCTIVITY OF SOIL
FIG. 2. DETAIL OF HEATER ELEMENT WITH PERMEABLE JACKET AND LEAD WIRES

a, noninductive winding, 16 feet of no. 40 enameled copper wire; b, 15 cm. O. D. glass tube; c, section of $\frac{1}{8}$-inch plaster of paris jacket; d, section of glass tube with wire shown behind; e, outside face of jacket; f, impermeable plug (both ends) in glass tube; g, rubber-covered lead-off wires to Wheatstone bridge.

two pots, one containing Yolo fine sandy loam, a recent alluvial soil from the campus at Davis, and the other containing Holland fine sand, a primary soil from the Sierra foothills. The permanent wilting percentage and the field capacity of Yolo fine sandy loam were 9 and 17.5 per cent, respectively, and those of Holland find sand, 5.3 and 10.5 per cent. Four sunflower plants were grown in each pot. When they had become well established and could ex-

tract the available moisture between field capacity and permanent wilting percentage in about a week, readings were begun.

The machine used in making the readings duplicated the Shaw-Baver instrument as originally designed, with the exception that the dry-soil heater was replaced by several air-jacketed heaters that could be used alternately. Each air-jacketed heater was separated by insulation from the others. Having a number of these elements reduced the time necessary for cooling and stabilization of the circuit after each run. The results of the experiment are given in table 1.

TABLE 1

Results of tests of jacketed heater elements in Yolo fine sandy loam and in Holland fine sand

SOIL TYPE AND MOISTURE CONTENT	HEATER NUMBER	RESISTANCE CHANGE IN BRIDGE WITH CURRENT ON 2 MINUTES			
		*Trial 1	Trial 2	Trial 3	Trial 4
		ohms	ohms	ohms	ohms
Yolo fine sandy loam at field capacity..	3	.231	.219	.2285	.223
	15	.2255	.234	.2225	.225
	16	.218	.218	.221	.218
Holland fine sand at field capacity.....	1	.228	.2305	.2245	.238
	2	.240	.219	.218	.218
	13	.232	.218	.218	.220
	14	.235	.219	.2245	.216
Yolo fine sandy loam at permanent wilting percentage......................	3	.1775	.1825	.185	.189
	15	.185	.1875	.186	.185
	16	.182	.182	.1825	.191
Holland fine sand at permanent wilting percentage..........................	1	.175	.189	.182	..
	2	.179	.178	.185	..
	13	.160	.180	.180	..
	14	.171	.178	.180	..

* Each trial represents a completed cycle from moist to dry conditions, so that repeated moistening and drying of the soil and heater elements have taken place in both pots of soil.

The following conclusions may be drawn from the data in table 1. Regardless of the fact that the soil-moisture percentages for the limits—field capacity and permanent wilting percentage—are very different for the two soils, comparable readings resulted. This fact seems to indicate that the plaster-jacketed heater may be applied to other soils with some prospect of obtaining readings similar to those in table 1 for permanent wilting percentage and field capacity moisture contents. The plaster of paris jacket appears to be able to adjust itself to comparatively rapidly changing moisture content in the soil in the pots and should, therefore, be suitable for use in the field. Field experiments covering a much broader range of soils are in progress.

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THE NEUTRALIZATION OF ACID-FORMING NITROGENOUS FERTILIZERS IN RELATION TO NITROGEN AVAILABILITY AND SOIL BASES

(A REPORT OF WINDSOR LYSIMETER SERIES D)

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A previous experiment with nitrogenous fertilizers on four soils of varying physical and chemical properties, under lysimeter conditions (Windsor lysimeter series A), has been reported elsewhere.[1] Differences in the effects of acid-forming fertilizers were observed on the soils under study, and it was suggested that this performance was conditioned by the extent of base-depletion (or degree of acidity) that had been attained in the soil prior to the application of the treatment. In the spring of 1934, the 9-inch lysimeter tanks used to contain the soils in the aforementioned experiment became available for a more detailed study of such relationships. The plan involved a comparison of two soils, differing chiefly in initial base status, one strongly acid and the other reasonably well supplied with calcium, magnesium, and other exchangeable bases. Three typical acid-forming fertilizer materials (sulfate of ammonia, urea, and cottonseed meal) were compared on each soil, with and without neutralization of potential acid-forming capacity of the treatment. The experiment was conducted under uncropped conditions, from May, 1934, to April, 1939.

A progress report of this experiment, by Morgan and Bailey[2], summarized results during the first 2 years. The present publication represents a complete report of all phases of the work, including studies of the soils after 5 years in the lysimeter tanks, under the various treatments.

METHODS OF STUDY

The general features of the lysimeter installation at Windsor have been described in previous publications. A series of 34 cylindrical tanks, 20 inches in diameter and 9 inches deep, were used for this experiment.

These tanks were filled with soils from plots in a liming experiment conducted on the "Pomeroy" field of the Tobacco Substation from 1930 to 1933, inclusive. The first, hereafter designated as "soil *a*," represented the surface soil (to plow depth) of plot L 9 in that experiment. This had received no lime. The other, "soil *b*," was collected from plot L 13. This had received dolomitic

[1] Morgan, M. F. 1936 Soil changes resulting from nitrogenous fertilization: a lysimeter study. Conn. Agr. Exp. Sta. Bul. 384.

Morgan, M. F., and Street, O. E. 1939 Seasonal water and nitrate leachings in relation to soil and source of fertilizer nitrogen. Conn. Agr. Exp. Sta. Bul. 429.

[2] Morgan, M. F., and Bailey, E. M. 1938 Evaluation of the influence of nitrogenous fertilizers on the acid-base status of soils by lysimeter studies. *Soil Sci.* 45: 387–400.

hydrated lime at the rate of 1,875 pounds per acre in 1930, and at the rate of 390 pounds in 1933, supplying approximately 745 pounds of calcium and 440 pounds of magnesium per acre in the two treatments. Both soils were Merrimac sandy loam. Although occurring less than 100 feet apart in the field, soil b was slightly coarser in texture and lower in initial nitrogen and organic matter content than soil a.

An equal number of tanks were filled with each soil, which was thoroughly mixed and distributed so as to provide the equivalent of 119 pounds of dry soil in each tank. After allowance for coarse sand and fine gravel, this represented approximately 2,300,000 pounds per acre of material less than 2 mm. in diameter. The differences in the two soils did not measurably affect their volume weights. The characteristics of the two soils, represented by the samples taken at the time of filling the tanks, are indicated in various tables in comparison with samples taken after 5 years of treatment.

Plan of treatment

Nitrogenous fertilizers, as employed in the management of soils for tobacco and other intensively fertilized crops in the Connecticut Valley, are applied in combination with other plant nutrients. In this experiment it was considered advisable to provide a constant, favorable level of other constituents, except those involved in the comparisons, through the addition of other materials not known to have any significant direct effect upon the soil reaction. Annual treatments in duplicate on each soil (except in the case of "no nitrogen") were as follows:

Nitrate of soda, including other neutral materials (monocalcium phosphate, sulfate of potash, gypsum, and magnesium sulfate).

Sulfate of ammonia (full acid effect), including monoammonium phosphate, to supply the needed amount of phosphorus; sulfate of potash, and magnesium sulfate.

Sulfate of ammonia (one-half neutralized), with basic materials sufficient to neutralize all acidity developed from the sulfate radical, as follows: precipitated bone, carbonate of potash, magnesium carbonate, and calcium carbonate.

Sulfate of ammonia (neutralized), including, in addition, calcium carbonate equivalent to acid production through nitrification.

Urea (full acid effect), including other neutral materials, as used with nitrate of soda.

Urea (neutralized), including, in addition, calcium carbonate equivalent to acid production through nitrification.

Cottonseed meal (full acid effect), including other materials as used with nitrate of soda. (In order to supply amounts of sulfate equivalent to other treatments, a small quantity of sodium sulfate was included.)

Cottonseed meal (neutralized), including, in addition, calcium carbonate equivalent to acid production through nitrification.

No nitrogen, including other materials as used to supplement the nitrate of soda treatment.

The amounts of the various elements added in these treatments during the 5 years are summarized in table 1. This also indicates the amounts supplied through atmospheric precipitation, based on data obtained from rain water

collections during the same period from duplicate open tanks adjacent to the lysimeters.

The theoretical net acid or basic effects of the total additions to the soil may be calculated from the amounts of the various constituents, expressed in terms

TABLE 1

Quantities of various elements* added by treatments and by rainfall to lysimeter series D, 5-year period, 1934–1939

In pounds per acre

TANKS	TREATMENTS	Ca	Na	S	Cl
1, 2, 17, 18	Nitrate of soda	1019	1702	1280	135
9, 10, 25, 26	Sulfate of ammonia (full acid)	124	54	1703	134
3, 4, 19, 20	Sulfate of ammonia ($\frac{1}{2}$ neutralized)	1019	54	1280	96
11, 12, 27, 28	Sulfate of ammonia (neutralized)	2357	54	1280	96
5, 6, 21, 22	Urea (full acid)	1019	54	1280	123
13, 14, 29, 30	Urea (neutralized)	2321	54	1280	123
7, 8, 23, 24	Cottonseed meal (full acid)	1019	273	1280	118
15, 16, 31, 32	Cottonseed meal (neutralized)	2203	273	1280	118
33, 34	No nitrogen	1019	54	1280	123
	Atmospheric precipitation†	124	54	138	96

* N added to all tanks (except 33 and 34), 1014 pounds per acre, including 14 pounds from atmospheric precipitation; P, to all tanks, 218 pounds; K, to all tanks, 880 pounds, including 50 pounds from atmospheric precipitation; and Mg to all tanks, 188 pounds, including 29 pounds from atmospheric precipitation.

† Included in above data.

of *calcium carbonate* equivalence, in pounds per acre. The results of these computations were as follows, for the various treatments during the 5-year period:

Nitrate of soda...Neutral

Sulfate of ammonia
    Full acid effect.. 14,260 acid
    One-half neutralized....................................... 7,084 acid
    Neutralized... 207 basic

Urea
    Full acid effect.. 7,153 acid
    Neutralized.. 23 acid

Cottonseed meal
    Full acid effect.. 6,187 acid
    Neutralized.. 345 basic

No nitrogen... 46 basic

The slight discrepancies, as compared with the original plan, were due to errors in initial estimates as to the composition of some of the materials. For all practical purposes, however, the figures are in accord with the plan of the experiment.

Conduct of the experiment

On May 26 of each year, the treatments were thoroughly mixed with the upper 2 or 3 inches of soil in the tanks. The soil surface was kept free from weeds by occasional light cultivation.

The drainage water was measured, after each period of precipitation causing leaching, and was sampled for subsequent analysis. The details of chemical study of this water were as outlined for lysimeter series A.[3]

At the conclusion of the fifth year, in April, 1939, the soils were removed from the tanks and carefully sampled. Soil studies involving these samples, by methods employed in series A, are summarized in various tables.

SEASONAL DISTRIBUTION OF LEACHING

The 5-year period covered by this experiment was marked by a generally more abundant precipitation than the previous period involving lysimeter series A. Marked differences in the amounts and distribution of rainfall from year to year, however, affected the quantities of drainage water passing through the soil. Table 2 shows the monthly precipitation and leachings.

The first year, a fairly dry one, gave some June leaching. Heavy fall rains thoroughly flushed the soil. The rest of the year was unusually dry, except for a warm, wet January. The second year, abundant but not excessive early summer rainfall caused moderate leaching. Further leaching of considerable magnitude occurred in September, November, and January. The spring thaw and a wet March produced large drainage water collections. The dry summer of 1936 produced little leaching until the fall months. Moderately mild, wet weather in early winter favored soil leaching. The summer of 1937 was generally wet, especially in August, which yielded an unusually large collection of drainage water. A wet fall caused frequent leaching. The winter was dry, followed by a spring of normal rainfall and moderate drainage. The summer of 1938 was unusually wet, causing severe depletion of soluble material from the soil through the heavy leachings of June and July. Following a dry August, the phenomenally high September rainfall, culminating in the hurricane of September 21, caused such an accumulation of drainage water in the collecting vessels that approximately 3 inches were lost, as nearly as could be estimated. It is reasonable to believe that this caused no appreciable error in the measurement of constituents thus removed from the soil, since the later leaching collections during the week preceding the hurricane contained not more than 2 p.p.m. of nitrate nitrogen from any treatment. Further heavy rainfall and leaching in early winter and in early spring brought the drainage water for the year to an unusually high total.

The proportion of precipitation represented as leaching varied considerably from year to year. The average seasonal excess of precipitation over leaching indicated rates of evaporation from the soil in general agreement with those

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[3] See Morgan, footnote 1.

TABLE 2

Atmospheric precipitation and drainage data from lysimeter series D, 1934–1939

In inches

		1934–35	1935–36	1936–37	1937–38	1938–39	AVERAGE 5 YEARS
June	Precipitation	3.47	5.53	2.75	5.63	7.00	4.87
	Leachings	1.21	0.55	0.07	0.97	2.05	0.97
July	Precipitation	3.20	4.30	2.45	4.40	8.54	4.58
	Leachings	0	0.83	0.15	0	5.62	1.32
August	Precipitation	3.45	1.80	4.35	6.81	2.11	3.70
	Leachings	0.51	0	0.74	2.03	0.14	0.68
September	Precipitation	8.63	4.78	3.86	4.33	12.63	6.85
	Leachings	5.53	2.46	1.51	2.86	9.05*	4.28
October	Precipitation	2.11	0.43	3.92	4.62	1.83	2.58
	Leachings	0	0	1.68	1.63	0	0.66
November	Precipitation	2.17	4.13	1.14	6.02	3.95	3.48
	Leachings	0.73	2.00	0.10	5.38	0.42	1.72
December	Precipitation	2.75	0.82	5.65	1.67	3.65	3.91
	Leachings	0	0	3.00	0.44	4.42	1.57
January	Precipitation	4.02	5.80	5.58	4.39	2.79	4.52
	Leachings	3.12	2.52	5.64	0	0.84	2.42
February	Precipitation	2.74	2.21	1.69	1.85	2.17	2.13
	Leachings	0	0	0	1.40	0	0.28
March	Precipitation	1.49	5.98	3.06	1.49	4.59	3.32
	Leachings	1.67	4.63	3.62	1.15	5.38	3.29
April	Precipitation	1.28	3.38	3.82	4.44	4.39	3.46
	Leachings	0	1.67	0	1.07	2.00	0.95
May	Precipitation	1.40	2.38	4.09	4.21	0.95	3.25
	Leachings	.08	0	1.76	1.60	....	0.69
Year	Precipitation	36.71	41.54	42.36	49.86	54.60	46.65
	Leachings	12.85	14.66	18.27	18.53	29.92	18.83

* Including an estimated 3 inches lost through overflow of collecting vessels.

presented in a previous publication[4] for the 1929–1934 period.   The apparent evaporation rates, thus obtained, were as follows:

	inches/day
June, July, and August	0.112
September, October, and November	0.062
December, January, February, and March	0.052
April and May	0.071

[4] See Morgan and Street, footnote 1.

Drainage water collections were substantially the same from both soils in spite of the fact that one was slightly more sandy than the other. On both soils, the cottonseed meal treatment caused consistently greater summer and fall leachings than did the other treatments. The apparent decrease in evaporation caused by yearly applications of cottonseed meal, at the rate of approximately 3000 pounds per acre, represented 0.439 inch of water from June to November. (Because of the abnormal conditions, the drainage water data for the week including the hurricane of 1938 were not included in this comparison.) The differences due to cottonseed meal were not significant during the winter and spring months. The effects were most pronounced when summer rains caused leaching.

SEASONAL DISTRIBUTION OF NITROGEN LOSSES BY LEACHING

Since the rainfall during the summer months varied greatly in the different years, there were differences, after treatment, in the elapsed time required to remove larger amounts of nitrates from the soil. Thus, in 1936 leaching of nitrates from the soil under the nitrate of soda treatment was very light until late in August. On the other hand, in 1938, at least three quarters of the nitrate applications were leached from the surface soil within 5 weeks. It is of interest to note the following dates, prior to which 75 per cent or more of the nitrate nitrogen liberated yearly had been washed from the soils:

1934: All treatments—September 18; nitrate of soda—August 26
1935: All treatments—October 3; nitrate of soda—July 27
1936: All treatments—September 20
1937: All treatments—August 24; nitrate of soda, urea, and sulfate of ammonia, neutralized or one-half neutralized—August 13
1938: All treatments—July 25; nitrate of soda—June 30.

Ammonia nitrogen losses by leaching were measured only in the composite samples of the leachings by 6-month periods. Unless much leaching occurred during the summer months, as in 1937 and 1938, little ammonia was leached, even from the full-acid sulfate of ammonia treatments. The amounts of ammonia nitrogen leached during these last 2 years, from June to November (presumably chiefly from June to August), are shown in table 3.

It is to be noted that the amounts of ammonia leached from the sulfate of ammonia and urea treatments are very closely related to the soil reactions resulting from the treatments on the two soils. This signifies that the retarded nitrification at the lower pH values left a larger residue of ammonia to be subjected to leaching. In the case of cottonseed meal, more gradually ammonified than urea, nitrification kept the ammonia at a low level even under the more acid conditions.

The seasonal distribution of nitrate leachings as affected by the various treatments is summarized in table 4.

As would be expected, nitrates are leached most rapidly from the nitrate of soda treatments, in both soils. The leaching is more rapid for every correspond-

ing treatment on soil *b* than on soil *a*. This may be due in part to the slightly less retentive character of soil *b*. The major factor, however, is likely to be its less acid condition, which causes earlier nitrification. This theory is confirmed,

TABLE 3

Ammonia nitrogen in drainage water collections from lysimeter series D, June to November, 1937 and 1938

In pounds per acre

	1937	1938	AVERAGE, 2 YEARS	MEAN pH OF SOIL, 1937 AND 1938
Soil *a*				
Nitrate of soda....................	0.5	1.2	0.8	5.25
Sulfate of ammonia				
Full acid.......................	132.7	74.6	103.7	4.09
½ neutralized...................	44.8	20.1	32.5	4.44
Neutralized.....................	3.7	19.2	11.4	5.23
Urea				
Full acid.......................	32.1	19.6	25.9	4.55
Neutralized.....................	16.0	22.3	19.2	5.20
Cottonseed meal				
Full acid.......................	3.5	2.2	2.9	4.55
Neutralized.....................	2.0	1.7	1.9	5.36
No nitrogen......................	1.3	1.9	1.6	5.21
Soil *b*				
Nitrate of soda....................	0.9	1.9	1.4	6.25
Sulfate of ammonia				
Full acid.......................	117.7	35.1	76.4	4.28
½ neutralized...................	9.5	26.8	18.2	4.89
Neutralized.....................	1.4	1.4	1.4	6.21
Urea				
Full acid.......................	3.4	27.5	15.5	5.16
Neutralized.....................	0.5	1.8	1.2	6.14
Cottonseed meal				
Full acid.......................	1.0	1.0	1.0	5.09
Neutralized.....................	1.7	.23	1.5	6.55
No nitrogen......................	0.8	1.3	1.1	6.24

in every comparison between acid and neutralized nitrogen treatments, by the greater proportions of nitrates in the drainage water in the earlier periods from the neutralized treatments.

On the other hand, the total production of nitrates has been consistently

greater for corresponding treatments on the more acid soil *a* than on soil *b*.
Even without nitrogen treatment there is a material difference in favor of this
soil.   In general, the magnitude of this excess of nitrate production for soil *a*

TABLE 4

*Cumulative leaching of nitrate nitrogen from lysimeter series D, under various treatments, in
relation to total quantities leached during the year, 1934–1939 average*

| | PERCENTAGE OF TOTAL YEARLY LEACHING OF NITRATE NITROGEN | | | NITRATE NITROGEN LEACHED PER YEAR |
	Before July	Before September	Before December	
				lbs./A.
Soil *a*				
Nitrate of soda	32.6	76.3	97.4	277
Sulfate of ammonia				
Full acid	10.8	45.6	96.0	181
½ neutralized	16.9	60.0	96.7	203
Neutralized	24.6	66.2	97.3	203
Urea				
Full acid	22.2	64.6	97.0	219
Neutralized	25.7	65.4	97.1	208
Cottonseed meal				
Full acid	18.8	61.6	95.0	180
Neutralized	23.0	64.1	96.6	192
No nitrogen	17.2	50.0	88.0	74
Soil *b*				
Nitrate of soda	43.1	83.0	98.1	252
Sulfate of ammonia				
Full acid	13.1	57.5	96.4	179
½ neutralized	24.8	71.4	95.5	188
Neutralized	33.8	72.0	96.0	153
Urea				
Full acid	24.8	72.8	97.7	210
Neutralized	33.5	73.9	96.8	186
Cottonseed meal				
Full acid	23.9	64.7	96.3	168
Neutralized	24.7	67.2	94.1	166
No nitrogen	17.4	42.7	92.9	55

is similar for all treatments, except the neutralized sulfate of ammonia treat-
ment.   In this instance the very poor nitrate nitrogen production in the less
acid soil, with little leaching as ammonia nitrogen, in comparison with that

from the more acid treatments (see table 3), suggests that there has been gaseous loss of ammonia nitrogen. As shown later, this treatment failed to produce the residual effect upon the soil nitrogen that would be anticipated from so incomplete a recovery in the drainage water.

The rapid early leachings of large proportions of the nitrates produced by neutralized urea, particularly on the less acid soil *b*, indicates the acceleration of nitrate production from this material under only slightly acid conditions.

As in previous experiments, both the total amount and the rate of nitrate production from cottonseed meal are materially less than those from urea. Under the more acid conditions, the rate of nitrification from sulfate of ammonia is retarded but, when the soil reaction is more favorable, there is no consistent difference between the performance of urea and sulfate of ammonia in this respect.

TOTAL REMOVALS OF NITROGEN BY LEACHING FROM VARIOUS TREATMENTS

The amounts of both nitrate and ammonia nitrogen removed by the drainage water from the soils under various treatments are shown in table 5. This provides a measurement of nitrogen changes that may be expected in the soil, assuming that neither nitrogen fixation nor gaseous losses to the atmosphere had occurred.

In most cases, the net gains or losses have been of small magnitude. Substantial gains from cottonseed meal and from neutralized sulfate of ammonia on soil *b* are indicated. It is to be noted that the total recoveries of nitrogen from both sulfate of ammonia and urea are high on both soils. This is due in part to the considerable liberation of nitrogen from the soil itself, as indicated by the "no nitrogen" data.

RESIDUAL EFFECTS ON SOIL ORGANIC MATTER

The soil samples collected at the end of the experiment were carefully examined for total nitrogen and organic carbon. At least four replicate determinations were made on the samples from each of the duplicate tanks, to ensure maximum precision of measurement. The results are shown as table 6.

The analyses, as compared with the original samples, indicate net losses of both nitrogen and organic matter in all cases, though the losses have been least for both soils when nitrogen was applied as cottonseed meal. In all instances, the neutralization of the acid fertilizer has increased the losses of soil nitrogen, and in all but one case, accelerated the organic matter depletion.

The most conspicuous disagreement between the changes in soil nitrogen and the data of table 5 is shown by the neutralized sulfate of ammonia on soil *b* and, to a lesser degree, by neutralized urea on the same soil. As has been suggested, this could be explained on the assumption that gaseous losses of ammonia have occurred under the approximately neutral soil conditions in these instances. The soil changes fail to give any indication that nonsymbiotic nitrogen fixation has occurred on these soils. Soil *a* is too acid for the growth of *Azotobacter*, though the pH measurements for all neutralized or nonacid

TABLE 5

Total removals of nitrogen by leaching from lysimeter series D, during 5 years of nitrogen treatments, 1934–1939

In pounds per acre

	NITRATE NITROGEN			AMMONIA NITROGEN	TOTAL NITROGEN LEACHING	INCREASE OVER "NO NITROGEN" TREAT- MENT	COMPUTED NET GAIN (G) OR LOSS (L) FOR SOIL‡
	Cumula- tive total*	Sums of 6-month compo- sites†	Average				
Soil *a*							
Nitrate of soda..........	1402	1371	1387	8	1395	1020	381 L
Sulfate of ammonia							
Full acid..............	875	932	905	224	1129	754	115 L
½ neutralized..........	1010	1021	1015	74	1089	714	75 L
Neutralized...........	1015	1016	1016	27	1043	668	29 L
Urea							
Full acid..............	1094	1095	1094	61	1155	780	141 L
Neutralized...........	1044	1034	1039	48	1087	712	73 L
Cottonseed meal							
Full acid..............	893	903	898	11	909	534	105 G
Neutralized...........	952	969	958	7	965	590	49 G
No nitrogen.............	362	373	368	7	375	....	361 L
Soil *b*							
Nitrate of soda..........	1260	1263	1261	7	1268	1012	254 L
Sulfate of ammonia							
Full acid..............	889	899	894	165	1059	803	45 L
½ neutralized..........	925	955	940	40	980	724	34 G
Neutralized...........	752	778	765	7	771	515	243 G
Urea							
Full acid..............	1060	1044	1052	35	1087	831	73 L
Neutralized...........	932	928	930	6	936	680	78 G
Cottonseed meal							
Full acid..............	834	850	842	6	848	592	166 G
Neutralized...........	822	834	828	7	835	579	179 G
No nitrogen.............	273	226	250	6	256	....	242 L

* Of separate measurements for each period of leaching.

† Includes nitrites that may have developed in stored water despite addition of toluene.

‡ In reference to data in table 1.

treatments on soil *b* are generally above 6.0, the accepted critical point for this nitrogen-fixing organism.

Both nitrogen and organic carbon are consistently lower for soil *b* than for

TABLE 6

Soil changes with respect to nitrogen and organic matter in lysimeter series D during 5 years of various nitrogen treatments

	NITROGEN			CARBON CONTENT	ORGANIC MATTER	
	Content		Net Loss		Content	Net Loss
	per cent	*lbs./A.*	*lbs./A.*	*per cent*	*lbs./A.*	*lbs./A.*
Soil *a*						
Nitrate of soda..............	.0686	1578	299	1.045	41,434	3886
Sulfate of ammonia						
Full acid.................	.0795	1829	48	1.085	43,020	2300
½ neutralized.............	.0719	1654	223	1.078	42,742	2578
Neutralized..............	.0709	1631	246	1.023	40,562	4758
Urea						
Full acid.................	.0711	1635	242	1.064	42,188	3132
Neutralized..............	.0683	1571	306	1.022	40,522	4798
Cottonseed meal						
Full acid.................	.0754	1734	143	1.114	44,170	1150
Neutralized..............	.0747	1718	159	1.051	41,672	3648
No nitrogen................	.0710	1633	244	1.017	40,324	4996
Orignal soil..................	.0816	1877	....	1.143	45,320	....
Soil *b*						
Nitrate of soda..............	.0516	1187	262	0.952	37,747	4599
Sulfate of ammonia						
Full acid.................	.0556	1279	170	0.968	38,381	3965
½ neutralized.............	.0586	1348	101	1.006	39,888	2458
Neutralized..............	.0517	1189	260	0.973	38,579	3767
Urea						
Full acid.................	.0580	1334	115	0.973	38,579	3767
Neutralized..............	.0570	1311	138	0.968	38,381	3965
Cottonseed meal						
Full acid.................	.0624	1435	14	1.023	40,562	1784
Neutralized..............	.0594	1362	87	1.031	40,879	1467
No nitrogen................	.0523	1203	246	0.975	38,654	3692
Original soil.................	.0630	1449	....	1.068	42,346	....

corresponding treatments on soil *a*, as would be expected from the initial differences in the soils. The wider carbon-nitrogen ratio of soil *b* is a characteristic for which there is no evident explanation, especially when one considers the

former close proximity of the soils in the field and the apparent uniformity of the area. Charcoal was not in evidence in either soil.

TABLE 7

Total leaching of various constituents other than nitrogen from lysimeter series D during 5 years, 1934–1939

In pounds per acre

	CAL-CIUM	MAGNE-SIUM	POTAS-SIUM	SODIUM	ALUMI-NUM	MANGA-NESE	SULFUR	CHLO-RINE	PHOS-PHORUS
Soil *a*									
Nitrate of soda............	1060	217	892	1523	3.4	10	1208	132	.38
Sulfate of ammonia									
Full acid...............	1028	276	1011	66	189	123	1476	131	.31
½ neutralized	1553	232	966	71	44	69	1112	88	.14
Neutralized.............	1985	202	810	55	12	27	1156	83	.30
Urea									
Full acid...............	1568	261	1045	62	63	77	1134	120	.24
Neutralized.............	1886	208	910	59	7	27	1088	105	.10
Cottonseed meal									
Full acid...............	1495	252	1043	263	7	29	1206	109	.27
Neutralized.............	1813	202	941	262	1	6	1226	103	.21
No nitrogen...............	1042	219	838	67	...	1	1141	111	.40
Soil *b*									
Nitrate of soda............	994	319	700	1549	...	...	1154	118	.54
Sulfate of ammonia									
Full acid...............	1189	398	1077	71	78	61	1458	115	.48
½ neutralized..........	1578	353	844	68	4	13	1152	88	.18
Neutralized.............	1625	315	670	51	...	...	1113	83	.17
Urea									
Full acid...............	1623	388	924	58	2	8	1056	120	.26
Neutralized.............	1827	340	755	57	...	...	1115	109	.32
Cottonseed meal									
Full acid...............	1441	366	898	261	...	...	1184	108	.24
Neutralized.............	1662	345	758	235	...	...	1200	108	.42
No nitrogen...............	951	335	728	61	...	...	1168	113	.19

LEACHING AND NET GAINS OR LOSSES OF VARIOUS CONSTITUENTS

The leaching of various constituents, other than nitrogen, during the 5 year period is summarized in table 7.

Comparison of these data with table 1 shows that constituents other than

phosphorus were leached in amounts approaching or somewhat exceeding their additions to the soil. As is usually the case, virtually no phosphorus was leached. Aluminum and manganese were removed from the soil in substantial amounts under the more acid treatments.

Net losses of calcium of considerable magnitude were evident under all of the acid fertilizers on both soils, especially the fully acid sulfate of ammonia. The neutralized treatments indicated net gains in calcium.

Magnesium losses, which were in excess of additions in all cases, were greater from the less acid soil, initially containing much more active magnesium, than from the more acid soil. The leaching of this constituent was accelerated also by the more acid treatments.

Potassium leachings from this sandy soil were in excess of the amounts in many of the treatments, especially under the acid nitrogenous materials. Neutralization of the fertilizers caused conservation of potassium.

Sodium removals in the drainage water were generally very close to the amounts measured in the atmospheric precipitation during the 5-year period. The slightly heavier soil a held back about 10 per cent of the sodium against leaching, as compared with 6 per cent for soil b.

Sulfur, uniformly supplied in large quantities as sulfates to attain the amounts supplied in sulfate of ammonia treatments, was not entirely removed by the drainage water. Larger residues were indicated under the more acid sulfate of ammonia treatment, supplied with somewhat more sulfur than normally (see table 1). The slightly smaller apparent net gain of sulfur under the cottonseed meal treatments suggests that more sulfur may have been added than was measured in the analyses of the materials applied, though the greater biological activity under this organic treatment may have contributed some of this element to the drainage water through the sulfofication of natural sources of sulfur in the soil.

Chlorine leachings were nearly, but not quite, equal to the amounts computed as additions through rainfall and impurities in the materials, with no consistent relationships to soil or treatment.

DIRECT MEASUREMENT OF SOIL CHANGES WITH RESPECT OF BASIC CONSTITUENTS

The exchangeable bases in the soil samples collected at the conclusion of the 5-year period were measured by the neutral ammonium acetate extraction method. To facilitate comparison with previous tables, these data are expressed in terms of pounds per acre in table 8. The net effects upon the exchangeable bases of the soil generally indicate that amounts leached in excess of additions are effective in depleting the soil from this standpoint, whereas residues from the treatments are effective either in increasing the exchangeable base status or in partly checking the losses.

The depletion of exchangeable calcium by the full acid effects of sulfate of ammonia is not so great as the losses of calcium suffered by leaching would indicate. On the other hand, the extra calcium applied in the neutralizing

TABLE 8

Basic constituents extractable with ammonium acetate from soils removed from lysimeter series D at end of 5 years, and net gains (G) or losses (L) thus indicated

In pounds per acre

	CALCIUM		MAGNESIUM		POTASSIUM		SODIUM	
	Final	Net change	Final	Net change	Final	Net change	Final	Net change
Soil *a*								
Nitrate of soda..........	737	38 G	42	11 L	854	114 G	138	85 G
Sulfate of ammonia								
Full acid..............	161	538 L	36	17 L	261	479 L	100	47 G
½ neutralized..........	304	395 L	39	14 L	432	308 L	106	53 G
Neutralized...........	549	150 L	42	11 L	522	218 L	106	53 G
Urea								
Full acid..............	300	399 L	36	17 L	423	317 L	106	53 G
Neutralized...........	562	137 L	45	8 L	566	174	69	16 G
Cottonseed meal								
Full acid..............	254	445 L	45	8 L	369	371 L	95	42 G
Neutralized...........	844	145 G	53	.....	468	272 L	79	26 G
No nitrogen..............	373	323 L	50	3 L	566	174 L	42	11 L
Original soil.............	699	.....	53		740	.....	53	
Soil *b*								
Nitrate of soda..........	848	92 L	81	87 L	953	362 G	79	58 G
Sulfate of ammonia								
Full acid..............	60	880 L	14	154 L	297	294 L	11	10 L
½ neutralized..........	263	677 L	48	120 L	423	168 L	21	.....
Neutralized...........	1070	130 G	64	104 L	629	38 G	16	5 L
Urea								
Full acid..............	323	617 L	28	140 L	396	195 L	21	.....
Neutralized...........	862	78 L	59	109 L	486	105 L	11	10 L
Cottonseed meal								
Full acid..............	254	686 L	31	137 L	369	222 L	16	5 L
Neutralized...........	1475	535 G	56	112 L	629	38 G	26	5 G
No nitrogen..............	839	101 L	70	98 L	791	200 G	26	5 G
Original soil.............	940	.....	168	.....	591	.....	21	.....

treatments, except cottonseed meal on the less acid soil *b*, has not increased the exchangeable calcium to the degree expected.

Magnesium losses by leaching are reflected in the soil, but not in full measure.

In comparison with soil a the greater removal of this constituent by the drainage water from soil b has resulted in a greater net loss of exchangeable magnesium.

Changes in exchangeable potassium are somewhat abnormal. Greater net losses from soil a than from soil b are associated with greater leaching of that constituent from this soil. Except for the nitrate of soda treatment, in which the soil gain is greater than would be expected from the lysimeter data, the results generally indicate considerable fixation of potassium added in the treatment, causing depletion of exchangeable potassium in excess of net losses, and in some instances, when less is leached than is added to the soil.

The exchangeable sodium data indicate smaller increases from the nitrate of soda treatment than from the remainder of sodium not leached. The apparent net gain in exchangeable sodium under most other treatments, though of small magnitude, is not evidenced by the lysimeter data.

EFFECTS OF ACID AND NEUTRAL TREATMENTS ON SOIL ACIDITY

Soil samples collected from each tank during the late fall or early spring of each year of the experiment were tested for pH by the glass electrode method. The results of the pH tests, based on averages for the replicate tanks, are given in table 9.

Except for an initial increase in pH, reactions have been kept at substantially the original level by the neutral treatments. The neutralized cottonseed meal, toward the end of the experiment, produced some decrease in acidity on both soils.

The fully acid sulfate of ammonia applications rapidly increased the acidity of both soils. The less acid soil b became as acid in 5 years as soil a after 3 years of treatment. The last 2 years of treatment were the least effective on both soils.

As would be expected, the half neutralized sulfate of ammonia and the acid urea and cottonseed meal applications were not substantially different in their residual effects upon the pH. All three treatments produced progressive and fairly steady increases in the acidity of both soils.

A more comprehensive evaluation of the effects of the various treatments on soil acidity is obtained from the details of the base-exchange studies on the samples collected at the end of the 5-year period, in relation to the original samples at the time of filling the tanks. These data are shown in table 10.

The base-exchange capacities represent averages of the values determined by ammonia replacement, using the method of Pierre and Scarseth, and by a barium-saturation procedure developed at this laboratory. The latter results were somewhat higher, approximating the sum of exchangeable hydrogen measured by barium replacement and the separately determined exchangeable bases by the ammonium acetate extraction.

The equivalent totals of the exchangeable bases show the combined effects of the treatments in a very consistent pattern. The exchangeable hydrogen evaluates the extent of depletion of the soil by the acid treatments. In most

cases, the final pH of the soil (see table 9) is in excellent agreement with the base-exchange status of the soil, though the pH for the "no-nitrogen" treatment on soil a is higher at the end of the experiment than would be thus indicated.

TABLE 9

Annual pH measurements of soils under acid and neutral nitrogenous fertilizer treatments, lysimeter series D, 1934–1939

	YEAR OF EXPERIMENT				
	1st	2nd	3rd	4th	5th
Soil a (initial test—5.20)					
Nitrate of soda.................	5.67	5.41	5.35	5.31	5.18
Sulfate of ammonia					
Full acid......................	4.81	4.30	4.26	4.14	4.05
½ neutralized.................	5.24	4.62	4.55	4.48	4.39
Neutralized..................	5.56	5.15	5.29	5.28	5.18
Urea					
Full acid......................	5.26	4.85	4.79	4.65	4.46
Neutralized..................	5.70	5.19	5.30	5.24	5.16
Cottonseed meal					
Full acid......................	5.35	4.95	4.77	4.70	4.40
Neutralized..................	5.61	5.40	5.46	5.35	5.47
No nitrogen....................	5.57	5.47	5.20	5.17	5.25
Soil b (initial test—6.32)					
Nitrate of soda.................	6.48	6.26	6.25	6.27	6.22
Sulfate of ammonia					
Full acid......................	5.26	4.86	4.42	4.30	4.25
½ neutralized.................	5.87	5.35	5.11	4.91	4.86
Neutralized..................	6.69	6.13	6.18	6.23	6.18
Urea					
Full acid......................	5.89	5.42	5.26	5.18	5.11
Neutralized..................	6.58	6.17	6.31	6.27	6.01
Cottonseed meal					
Full acid......................	6.08	5.66	5.42	5.28	4.89
Neutralized..................	6.76	6.19	6.36	6.43	6.66
No nitrogen....................	6.26	6.19	6.25	6.28	6.20

EVALUATION OF NET ACID OR BASIC EFFECTS OF TREATMENTS

The results of this experiment show that soil changes in the acid or basic direction are not expressed solely in terms of calcium depletion or accumulation; they involve the other bases to a considerable degree. Exchangeable hydrogen

TABLE 10

Comparison of base-exchange data on original soils and on samples at the end of 5 years, lysimeter series D

Base exchange in m.e. per 100 gm. soil

	EXCHANGEABLE BASES					EX-CHANGE-ABLE H	BASE-EX-CHANGE CAPACITY	RELATIVE BASE SAT-URATION
	Ca	Mg	K	Na	Total			
								per cent
Soil *a*								
Nitrate of soda............	1.60	.15	.95	.26	2.96	2.99	5.95	49.8
Sulfate of ammonia								
Full acid..............	0.35	.13	.29	.19	0.96	4.79	5.75	16.7
½ neutralized...........	0.66	.14	.48	.20	1.48	4.16	5.64	26.2
Neutralized.............	1.19	.15	.58	.20	2.12	3.40	5.52	38.4
Urea								
Full acid..............	0.65	.13	.47	.20	1.45	4.15	5.60	25.8
Neutralized.............	1.22	.16	.63	.13	2.14	3.27	5.41	39.5
Cottonseed meal								
Full acid..............	0.55	.16	.41	.18	1.30	4.38	5.68	22.9
Neutralized.............	1.83	.19	.52	.15	2.69	2.81	5.50	48.9
No nitrogen...............	0.81	.18	.63	.08	1.70	3.68	5.38	31.6
Original soil..............	1.52	.19	.82	.10	2.63	3.04	5.67	46.4
Soil *b*								
Nitrate of soda............	1.84	.29	1.06	.15	3.34	1.56	4.90	68.2
Sulfate of ammonia								
Full acid..............	0.13	.05	.33	.02	0.53	4.23	4.76	11.1
½ neutralized...........	0.57	.17	.47	.04	1.25	3.62	4.87	25.7
Neutralized.............	2.32	.23	.70	.03	3.28	1.62	4.90	66.9
Urea								
Full acid..............	0.70	.10	.44	.04	1.28	3.40	4.68	27.4
Neutralized.............	1.87	.21	.54	.02	2.64	2.24	4.88	54.1
Cottonseed meal								
Full acid..............	0.55	.11	.41	.03	1.10	3.66	4.76	23.1
Neutralized.............	3.20	.20	.70	.05	4.15	1.06	5.21	79.6
No nitrogen...............	1.82	.25	.88	.05	3.00	1.57	4.57	65.6
Original soil..............	2.04	.60	.65	.04	3.33	1.33	4.66	71.5

is also a measurement of the extent to which the base-exchange capacity is depleted. It is convenient, however, to evaluate the net effects of a treatment in terms of equivalent amount of calcium carbonate per acre, since limestone,

chiefly calcium carbonate, is the most common material employed in soil acidity adjustment.

TABLE 11

Evaluation of net changes in base status of soils in lysimeter series D during the 5-year period, 1934–1939

Expressed as calcium carbonate equivalence, in pounds per acre (B—more basic, A—more acid)

	FROM BASE-EXCHANGE DATA		FROM LYSIMETER DATA		AVERAGE ALL EVALUATIONS
	Exchangeable bases	Exchangeable hydrogen	Not including Mn and Al	Including Mn and Al	
Soil *a*					
Nitrate of soda..................	380 B	58 B	150 B	116 B	176 B
Sulfate of ammonia					
Full acid.....................	1921 A	2012 A	2806 A	4083 A	2706 A
½ neutralized.................	1323 A	1288 A	1668 A	2036 A	1579 A
Neutralized..................	586 A	414 A	966 B	851 B	204 B
Urea					
Full acid.....................	1357 A	1277 A	1898 A	2381 A	1728 A
Neutralized..................	564 A	265 A	955 B	863 B	247 B
Cottonseed meal					
Full acid.....................	1530 A	1541 A	1633 A	1725 A	1607 A
Neutralized..................	69 B	265 B	863 B	748 B	486 B
No nitrogen....................	1070 A	736 A	150 A	150 A	526 A
Soil *b*					
Nitrate of soda..................	12 B	265 A	35 A	35 A	81 A
Sulfate of ammonia					
Full acid.....................	3220 A	3335 A	3830 A	4370 A	3689 A
½ neutralized.................	2392 A	2634 A	2151 A	2207 A	2346 A
Neutralized..................	58 A	334 A	1576 B	1576 B	690 B
Urea					
Full acid.....................	2392 A	2381 A	2392 A	2415 A	2395 A
Neutralized..................	794 A	1047 A	771 B	771 B	75 A
Cottonseed meal					
Full acid.....................	2564 A	2680 A	1794 A	1794 A	2208 A
Neutralized..................	943 B	311 B	943 B	943 B	785 B
No nitrogen....................	380 A	276 A	242 A	242 A	285 A

Earlier in this publication the theoretical capacities of the various treatments for increasing or overcoming acidity were presented on this basis. It is now pertinent to measure the extent to which these effects have been expressed under the conditions of this experiment.

The net acid or base effects, as computed from the lysimeter data and as measured by base-exchange studies, are shown in table 11. This includes a column based on the assumption that manganese and aluminum leached from the soil also tend to increase the residual acidity of the soil, an assumption that may be subject to question from a theoretical standpoint. It indicates to a degree, however, the effect that the treatment might have if subsurface soil were also involved, as in natural conditions.

It is evident that, from any standpoint, the full effects of the acid treatments have not been manifested on either soil; however, the less acid soil b has been influenced to a greater degree.

TABLE 12

Residual effects of acid and neutral nitrogen fertilizers, as measured by growth of alfalfa in pot cultures, on soils from lysimeter series D, after 5 years of treatment

TREATMENTS	ALFALFA YIELD, DRY WEIGHT PER POT	
	Soil *a*	Soil *b*
	gm.	*gm.*
Nitrate of soda......................	6.4	12.3
Sulfate of ammonia		
Full acid...........................	*	*
½ neutralized.......................	4.3	3.4
Neutralized........................	23.7	20.6
Urea		
Full acid...........................	1.9	3.3
Neutralized........................	23.8	15.3
Cottonseed meal		
Full acid...........................	*	*
Neutralized........................	28.1	21.8
No nitrogen.........................	4.6	15.5

* Complete failure.

On the other hand, when the acid or basic treatments have been applied in combination with amounts of calcium carbonate corresponding to their acid potentialities, the net effects upon the soils have been substantially as expected.

Nitrate of soda has not materially affected the net base status of the soil under uncropped conditions. This is in harmony with the theory that, when the crop is not involved, the residual effect of such a material is neutral under conditions of normal soil leaching.

RESIDUAL EFFECTS UPON GROWTH OF AN ACID-SENSITIVE CROP

Portions of the soils removed from the various lysimeter tanks in April, 1939, were placed in 2-gallon glazed earthenware pots and removed to the greenhouse at New Haven. Alfalfa was seeded in each pot, without further soil treatment

except watering. Two clippings were harvested, except where the crop failed to grow beyond the early seedling stage. The results of this experiment are shown in table 12.

In view of the well-known acid-sensitiveness of alfalfa, the crop failures or poor yields after the more acid treatments are to be expected. Two features of the results, however, are somewhat phenomenal.

First, it is to be noted that, after the acid cottonseed meal treatments, crop failures, almost as decisive as those following the fully acid sulfate of ammonia applications during the 5 years, were obtained in both soils. On the other hand, yields were obtained following the acid urea and the half neutralized sulfate of ammonia treatments, both substantially as acid in their effects upon the soil. It is to be noted, however, that the residual exchangeable calcium was somewhat higher under these last two treatments (see table 8).

Second, after the neutralized treatments on the more acid soil, excellent growth of alfalfa was obtained at pH values generally considered very unfavorable for this crop (see table 9). Actually, these yields were better than after any of the nonacid treatments on soil *b*. Such results are more in line with the basic residues indicated by lysimeter data (table 11) than with the base-exchange trends in these instances. The poorer yields on soil *b*, for corresponding treatments, cannot be thus explained. It is possible that minor element deficiencies, associated with the greater degrees of neutralization, may have been involved.

SUMMARY

Comparisons were made of the effects of sulfate of ammonia, urea, and cottonseed meal, both with and without neutralization of theoretical acid production, and of nitrate of soda, applied to two soils differing in their initial base status, in lysimeter tanks without crop. Annual treatments of 200 pounds of nitrogen per acre in these materials were applied in combination with other materials supplying equal amounts of other constituents, except as required to adjust the acidity.

Drainage water studies provided a basis for the evaluation of both the rates of nitrogen transformation to nitrates and the total liberation of available nitrogen from these fertilizers, as affected by the soil and by neutralization by a liming material. The nitrates supplied as nitrate of soda were almost entirely leached from the surface soils used in the tanks within 6 weeks to 4 months, depending upon the conditions of summer rainfall occurring during the 5 years of these trials.

The rate of nitrification of the other materials was accelerated by the neutralizing treatments, as evidenced by the early leaching of larger proportions of the total annual nitrate production. The lime-adjusted urea treatment showed particularly high acceleration of nitrification on the less acid soil. The transformation of ammonia to nitrates under the fully acid sulfate of ammonia treatment was definitely retarded, particularly on the more acid soil. Neutralizing one half of the potential acidity of this treatment considerably favored nitrifica-

tion.   Cottonseed meal was more slowly nitrified than urea, both with and without neutralization, on both soils.

The total measurements of nitrates and ammonia nitrogen in the drainage water indicated a greater capacity for nitrate production on the more acid soil in most comparisons.   Nitrate production from sulfate of ammonia was definitely increased by partial neutralization.   On the other hand, when this material was fully neutralized in applications to the less acid soil, the considerably decreased nitrogen recovery suggested that some losses of ammonia to the atmosphere may have been engendered at a soil reaction approaching the neutral point. Measurements of nitrogen in the soil at the end of the experiment tended to confirm this view.   The neutralized urea treatment showed a similar tendency.

Ammonia nitrogen was leached in considerable amounts from sandy surface soils used in this experiment in years when heavy rains occurred early in the season.   Such ammonia losses were chiefly from the sulfate of ammonia and urea treatments.   They were smaller when these materials were neutralized. The less acid soil, although slightly more sandy, did not leach as much ammonia for corresponding treatments.

Since both soils liberated a considerable amount of nitrogen without additions of this element in the treatment, the total leachings of nitrogen produced net losses from the soil during the 5-year period in most instances.   From lysimeter data, cottonseed meal treatments should have produced small net gains of soil nitrogen in all comparisons.   The soil analyses indicated some nitrogen loss, even under this treatment, but these were of smaller magnitude than with the other nitrogen fertilizers.

Considerable amounts of the calcium added in the neutralizing treatments were not represented in the leaching.   Most of this apparent residue was not accounted for in measurements of the exchangeable calcium of the soils at the conclusion of the experiment.   On the other hand, net losses of calcium under the acid treatments were similarly evidenced by both leaching and soils data. This was also true of magnesium.   Except under the nitrate of soda treatments, potassium losses by leaching were of much smaller magnitude than the decreases in exchangeable potassium.   Other leachings were closely in line with the amounts supplied in the treatments, except for phosphorus, which did not leach.

Acid nitrogen fertilizers caused considerable leaching of aluminum and manganese, particularly when applied to the more acid soil.   After the first 2 years, the fully acid sulfate of ammonia treatment produced similar leachings of these constituents on both soils.

The less acid soil had been previously treated with dolomitic lime.   Hence, this soil leached more magnesium and less potassium for corresponding treatments, particularly in the earlier years of the experiment.   Calcium leachings from both soils were of similar magnitude, although one was much more acid than the other.

Lysimeter data, pH measurements, and base-exchange studies all show the acid effects of sulfate of ammonia, urea, and cottonseed meal upon both soils,

except when fully neutralized with lime.   The acid effects were more pronounced on the initially less acid soil, particularly from the fully acid sulfate of ammonia treatment.   The neutralization of approximately one-half of the potential acidity of this fertilizer gave similar results to those obtained from urea.

Increases in acidity due to strongly acid nitrogen fertilizers were measured by net base depletion, by leaching, by decreases in exchangeable bases, and by increases in exchangeable hydrogen.   These represented much smaller calcium carbonate equivalents than could be evaluated from the potential acidity of the treatment.   After the soil becomes strongly acid, further applications of an acid-reacting fertilizer produces but slight effects upon the base status of the soil.

On the other hand, amounts of lime applied in quantities equivalent to the acidity of the fertilizer serve to maintain the net base status of the soil at a fairly constant level, except when applied in connection with a less fully available nitrogen material, such as cottonseed meal.   The use of a liming material in neutralizing acid nitrogen fertilizer produces a change in the distribution of the various exchangeable bases.   Thus, in this experiment, an acid soil treated with "neutral" fertilizers for 5 years was made much more productive for alfalfa, a result believed to be associated with the changed proportions of the various bases.

STUDIES OF CLAY PARTICLES WITH THE ELECTRON MICRO-SCOPE: II. THE FRACTIONATION OF BEIDELLITE, NONTRO-NITE, MAGNESIUM BENTONITE, AND ATTAPULGITE[1]

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The advent of the electron microscope has placed in the hands of soil scientists a weapon of unique power. With it the shapes of the smallest particulate constituents of the soil can be made visible, since its practical resolving power has already approached 2 mμ and the theoretical limit has by no means been reached. It is particularly well adapted to the study of the clay minerals; first, in order to characterize them by their appearance, and second, to assess more exactly than has hitherto been possible the contribution of their crystal habit to other physical and chemical properties.

Several individual clay minerals have already shown highly characteristic features in their crystal habit (2, 7),[2] although further investigation of the range of habit possible within a given species is desirable. The present communication is concerned with four clay minerals; beidellite from Putnam clay; nontronite from Sandy Ridge, North Carolina; magnesium bentonite from Hector, California; and attapulgite from Attapulgus, Georgia.[3] In each case fractions of various settling velocities were examined. It is therefore possible to follow the relationship of settling velocity and linear dimensions, provided the particles are present as individuals. It is not difficult to distinguish between aggregates present in the original clay suspension and those formed by coagulation during evaporation on the nitrocellulose film that is used as a support.

The sodium-clay fractions used which fell within the range 2 μ–200 mμ (equivalent spherical diameter) were prepared by the two-layer method (3) in the tube centrifuge. The finer fractions were prepared by the more recently devised supercentrifuge procedure (8). Both methods, when used with well-dispersed systems, give clean fractions in one operation.

No acid treatment was used in preparing the nontronite, magnesium bentonite, and attapulgite for dispersion. Soluble substances and part of the exchangeable bases were removed by simple dialysis.

The electron micrographs were carefully selected so as to be representative

of the particular fractions concerned. A number of particles were measured to obtain an idea of the mean dimensions, from which settling velocities could be calculated. These were then compared with the known values for the fractions. In the finest fractions, in which the lower limit of settling velocity is not defined, measurements were made on particles that can be regarded as near the maximum size. In the platy particles, mean diameters were measured. Lath-like particles displayed two and sometimes all three of their principal dimensions. Since small errors (2–4 mμ when particles are in sharp focus) in measurement, inherent in the electron micrographs are of constant magnitude at the periphery of the object measured, they are relatively unimportant with larger particles. With decreasing particle size below 50 mμ the errors increase in importance. For this reason, thickness measurements of thin particles apparently on edge are of questionable significance. Even when these errors are disregarded, it is hazardous to measure thicknesses of particles apparently on edge. A plane surface 500 mμ in diameter, tilted at an angle of 1° with the vertical, would appear to have a thickness of 8.8 mμ. If the angle of tilt were 5°, the apparent thickness would be 43.7 mμ.

Throughout the series the linear dimension shown in the micrographs represents 1 μ. Measurements were made at magnifications around 40,000 diameters.

<div align="center">RESULTS</div>

<div align="center">*Beidellite*</div>

The beidellite fractions were prepared[4] from the B horizon of a Putnam profile in Boone County, Missouri. The two-layer method as applied to the Sharples supercentrifuge was used.

Fraction 100–50 mμ (fig. 1). The particles are well defined and obviously consist of plates. Interpretations regarding thickness may be based on electron penetration and differences in density where particles overlap. The mean of 24 measurements of particle diameters was 373 ± 21 mμ. This value may be compared with the dimensions determined indirectly (4) from the mean sedimentation velocity and the mean volume as obtained by ultramicroscopic count, namely, 470 mμ in diameter and 15 mμ thick. Thickness calculations based on the formula $v = \dfrac{2}{9} \dfrac{ab\,(D - d)g}{\eta F}$ previously discussed (3) for flattened ellipsoids of rotation settling in random orientation give values for $2\,a$ of 16 mμ. The mean settling velocity v is taken as 5.38×10^{-7} cm. per sec., the mean semidiameter b as found above is 1.86×10^{-5} cm., $(D - d)$ is taken as 1.40, g is 981, η is 0.0089 for water at 25°C., and F is 0.945. The value of a obtained by using these values is 8.0 mμ; the thickness of the particle, therefore, is 16 mμ. Perfect orientation parallel to b would give a much smaller value of $2a$, namely 9.6 mμ.

Fraction < 20 mμ (fig. 2). The mean diameter of 10 of the largest and best defined particles, whose settling velocity would therefore be close to the maximum for the fraction, is 75 ± 7 mμ. The value of the thickness calculated by

[4] By E. P. Whiteside.
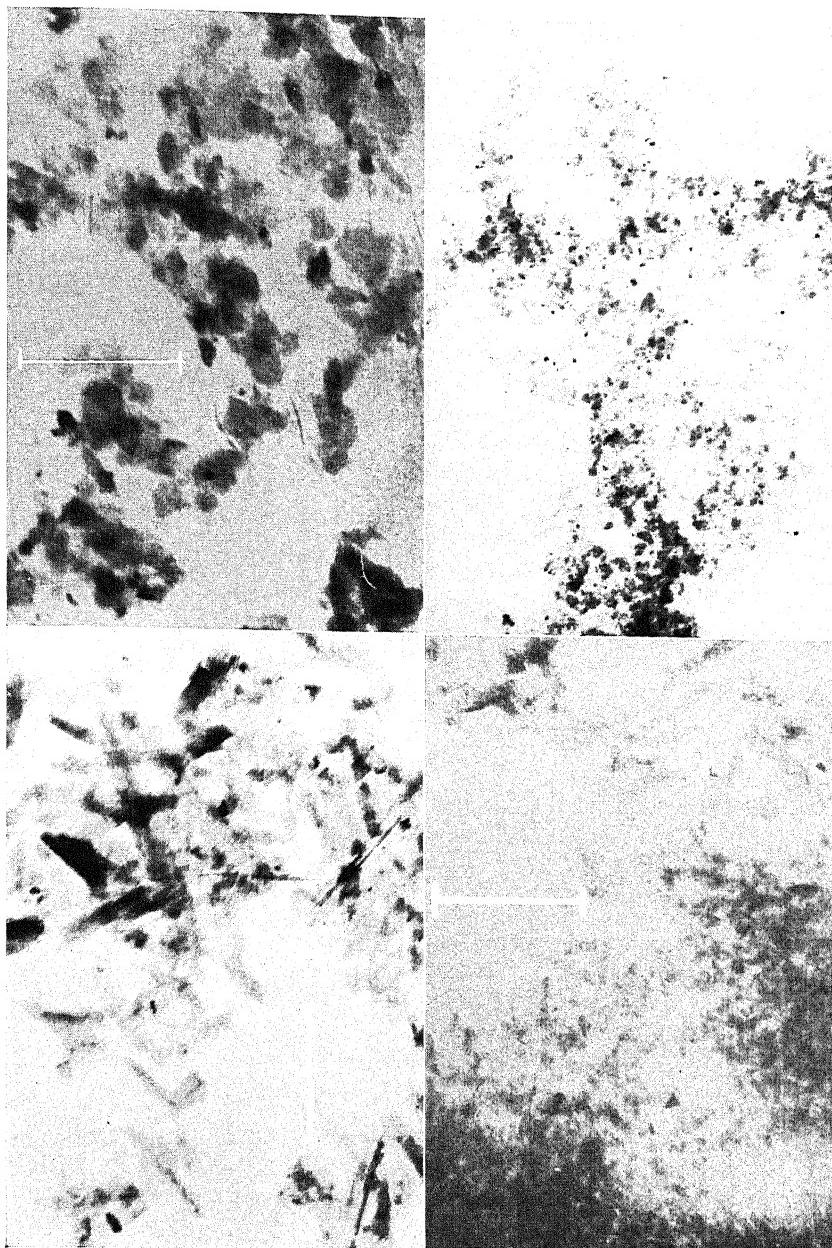
FIG. 1. (upper left) BEIDELLITE FRACTION 100–150 mμ IN EQUIVALENT SPHERICAL
DIAMETER
FIG. 2. (upper right) BEIDELLITE FRACTION < 20 mμ IN EQUIVALENT SPHERICAL
DIAMETER
FIG. 3. (lower left) NONTRONITE FRACTION 200–50 mμ IN EQUIVALENT SPHERICAL
DIAMETER
FIG. 4. (lower right) NONTRONITE FRACTION < 50 mμ IN EQUIVALENT SPHERICAL
DIAMETER

the foregoing formula is 5.0 mμ.   It is interesting to note that the volume of such a particle is 3.5 times that of a sphere of equivalent diameter 20 mμ.   In this particular clay there is no evidence that particles of smaller settling velocity are produced by micaceous cleavage alone from those of larger size.   Neither do particles in the fraction 100–50 mμ show a composite character such as might be expected if they were built up from units in the 20–5 mμ range.   The fractionation of this sodium clay evidently gives primary particles of various sizes and not a series of aggregates.   We may conclude that the mechanical analysis of this beidellite clay can justifiably be extended down to the smallest particles

Nontronite

It was found difficult to effect complete dispersion of the nontronite without pretreatment with acid, and under the ordinary microscope the 5–2 μ and 2–1 μ fractions were seen to be partly aggregated.   The electron microscope pictures of the 2–1 μ, 1–0.5 μ, and 0.5–0.2 μ fractions show large aggregated clumps of lath-like particles.   The individual laths were generally too small for the settling velocities of these fractions.   It was apparent from the micrographs that aggregates were present from the start.

Fraction 200–50 mμ (fig. 3).   Here the lath-like character was well shown, and some measurements of the thickness were ventured, despite the shortcomings of such measurements.   The mean length of ten particles measured was 567 $\pm$ 57 mμ, the mean width 108 $\pm$ 14 mμ, and the mean thickness of five particles apparently on edge 14 $\pm$ 3 mμ.   An exact calculation of the settling velocity of a particle having these dimensions is difficult.   It is easier, by using simplifying assumptions, to compare the known limits of settling velocity for this fraction, namely, 3.7 $\times$ 10^{-6} cm./sec. and 2.3 $\times$ 10^{-7} cm./sec., with those calculated.   If the particles are assumed to behave as plates whose mean diameter is $\dfrac{108 + 567}{2}$ mμ and whose thickness is 14 mμ, the simplified formula for flattened ellipsoids of rotation can be used as in the case of the Putnam fractions.   The calculated value is 8.9 $\times$ 10^{-7} cm./sec., which is within the limits for the fraction.   Alternatively, the particle can be assumed to settle like a rod, of length 567 mμ and mean thickness $\dfrac{108 + 14}{2}$ mμ.   Application of the more complicated formulas of Müller (5) shows the mean settling velocity for such a particle to be 3.0 $\times$ 10^{-7} cm./sec.   Both calculations lead to values nearer the lower than the upper limit of sedimentation velocity, and it is possible therefore that this fraction also may have possessed a certain degree of aggregation.

Fraction < 50 mμ (fig. 4).   The electron micrograph indicates a more even distribution of material than was found in the coarser fractions.   Measurements of ten well-defined lath-like particles gave a mean length of 305 $\pm$ 27 mμ and a mean width of 72 $\pm$ 8 mμ.   As particles of this size would have a settling velocity close to that of a spherical particle 50 mμ in diameter, this fraction was probably well dispersed originally.

Apart from the shape, one other feature of nontronite micrographs is worthy of note. Some of the particles show striations parallel to the length. These, coupled with an overlapping of laths, produce in the thinnest particles of aggregated masses a somewhat fluffy appearance, very evident in figure 3.

Magnesium bentonite

The swelling clay magnesium bentonite has also been called "magnesium beidellite" and is regarded as the "end member" of the saponite group. It is characterized by a low chemical stability, as shown by its complete decomposition during electrodialysis. The fractions separated in the centrifuge as the sodium clays were therefore purified by simple dialysis; hence the suspensions used were sodium-hydrogen clays.

All except the finest fraction gave electron micrographs showing the presence of irregular aggregates in the suspensions. The regularity of aggregate size in a given fraction establishes beyond question that the aggregation did not result from drying on the nitrocellulose film. This is especially noticeable in the 2–1 μ, 1–0.5 μ, and the 0.5–0.2 μ fractions. The individual particles are seen to be lath-like, as are those of nontronite. The magnesium bentonite laths, however, are much narrower, and the two minerals are easily distinguished.

Fraction 500–200 mμ (fig. 5). The dimensions as measured on ten particles apparently lying flat were: length 625 ± 98 mμ and width 63 ± 4 mμ. It is evident that aggregates were present during separation, since the settling velocity corresponding to a rod-shaped particle 625 mμ in length and 63 mμ in diameter is only 8.75 × 10^{-7} cm./sec., whereas that for a 200 mμ spherical particle is 2.9 × 10^{-6} cm./sec. The general appearance of the particles was that of thin laths rather than of circular or square section rods. This would make the discrepancy between the known limits of settling velocity and those calculated for single laths even more striking.

Fraction 200–50 mμ (fig. 6). The general appearance was similar to that of the 500–200 mμ fraction but with a more open aggregation. The measurements of ten particles gave: length 680 ± 220 mμ, width 67 ± 15 mμ. The linear dimensions therefore are not greatly different from those of the coarser fraction. If the thickness is assumed to be approximately 10 mμ, the settling velocity would be of the same order as that for a spherical particle 50 mμ in diameter. Figure 6 shows that both aggregates and single particles were concerned in sedimentation.

Fraction < 50 mμ (fig. 7). In appearance the individual particles were similar to those of the coarser fractions. Measurements of eight reasonably well defined particles gave: length 483 ± 68 mμ, width 61 ± 10 mμ.

These three fractions of magnesium bentonite all show instances of striations parallel to the long axis of the laths but the striations are fainter than those of nontronite. Magnesium bentonite differs from nontronite in showing a greater elongation of particles.

The striations in the micrographs of nontronite and magnesium bentonite, probably produced by electron diffraction in these crystals, may be the clue that
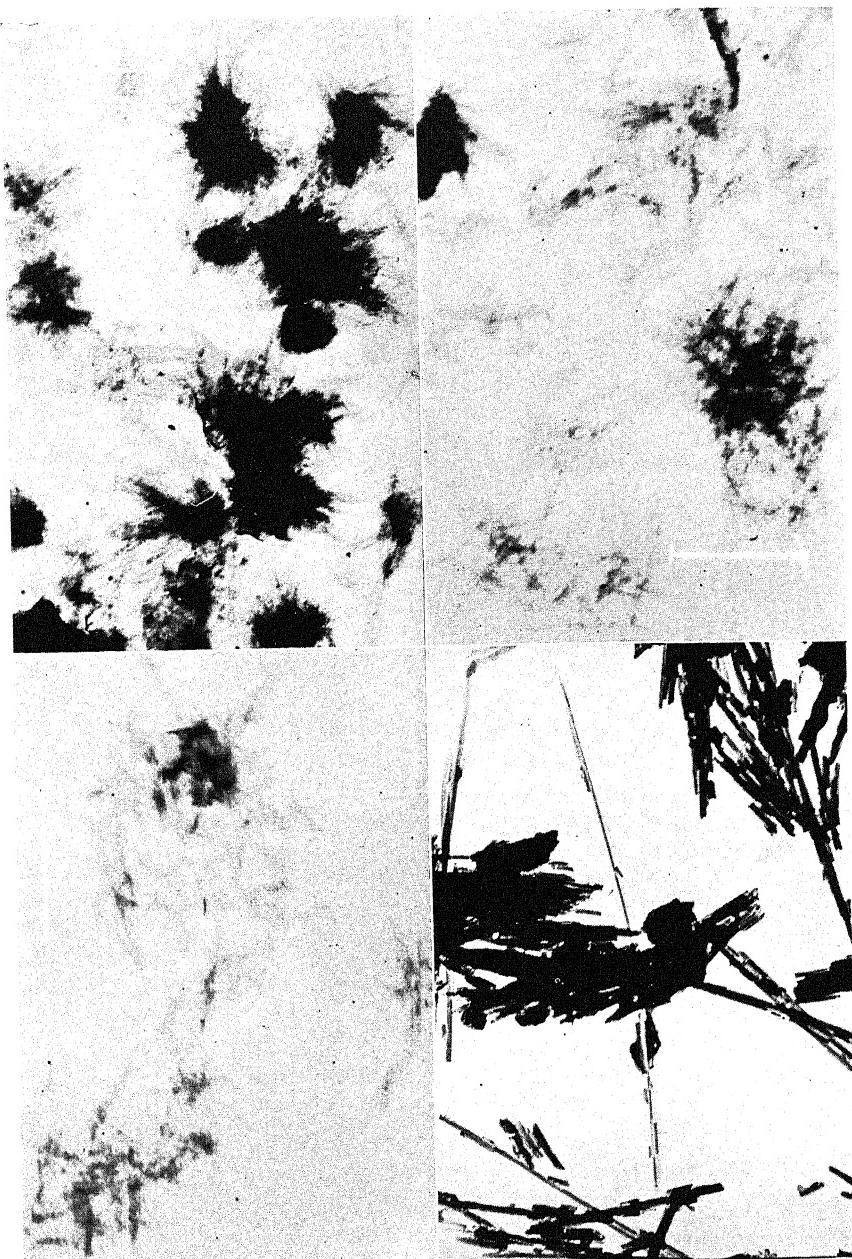
FIG. 5. (upper left) MAGNESIUM BENTONITE FRACTION 500–200 mμ IN EQUIVALENT
SPHERICAL DIAMETER
FIG. 6. (upper right) MAGNESIUM BENTONITE FRACTION 200–50 mμ IN EQUIVALENT
SPHERICAL DIAMETER
FIG. 7. (lower left) MAGNESIUM BENTONITE FRACTION < 50 mμ IN EQUIVALENT
SPHERICAL DIAMETER
FIG. 8. (lower right) SERPENTINE ASBESTOS

will give us the reason for structural differences between these minerals and montmorillonite, which does not show the striations.

Attapulgite

Attapulgite shows a striking resemblance to asbestos (fig. 8). Single fibers and bundles of fibers are interlaced in the presence of mineral impurities of entirely different habit. It was pointed out in the discussion of magnesium bentonite that aggregates shown in the electron micrographs existed in the original suspension. This fact is further emphasized by the constancy of single particle dimensions in the fractions 500–200 mμ, 200–50 mμ, and < 50 mμ. On first observation of the electron micrographs of attapulgite it may be thought that here, too, the aggregates existed in the suspension. In this case, however, particle widths have shown a decided decrease with decreasing settling velocities. It is unlikely, therefore, that aggregates were concerned in the original sedimentation.

Fraction 2 μ–500 mμ (fig. 9). Because of the smallness of the field only ten of the shorter single fibers could be measured; these had a mean length of 1.22 ± 0.12 μ and a mean width of 63 ± 7 mμ.

Fraction 500–200 mμ (fig. 10). The fibers comprising this fraction are similar to those of the preceding fraction except that many are seen to be made up of bundles of very thin units. The measured dimensions of five particles were: mean length 875 ± 66 mμ, mean width 42 ± 6 mμ. Rod-shaped particles of this size would have settling velocities (calculated by Müller's formulas) less than those of spherical particles of 200 mμ diameter. Thin fibers would settle even more slowly. It is apparent that existing formulas require modification. Work is in progress to establish the correct relationship.

Fraction 200–50 mμ (fig. 11). In this fraction it is apparent that larger particles separate along cleavage planes parallel to the length. Some of the particles that settled as individuals in the fractionation are for the most part bundles of thin, parallel fibers. These bundles are shorter than the individual fibers also present in this fraction. The mineral grains, which are clearly present as impurities, afford a satisfactory check on the mean settling velocity, since their mean diameters range from 120 to 170 mμ. Ten clay particles gave the following measurements: mean length 685 ± 100 mμ, mean width 22 ± 2 mμ.

Fraction <50 mμ (fig. 12). The single fibers clearly seen in this fraction are extremely thin. Close examination reveals that these fibers are crossed by still thinner fibers too thin to be distinguished from the nitrocellulose film. Their presence is established by increased density at points of intersection. The measurement of ten of the largest units gave: mean length 645 ± 45 mμ, mean width 17 ± 4 mμ. This fraction probably consisted during fractionation of some thin single fibers along with some bundles of these fibers.

The mineral impurity in this fraction brings to the front another phenomenon avoided in all previous considerations, namely, inferences regarding thickness of particles gained from the electron micrographs. The electron intensity was higher for the two smaller fractions of attapulgite than for any of the other
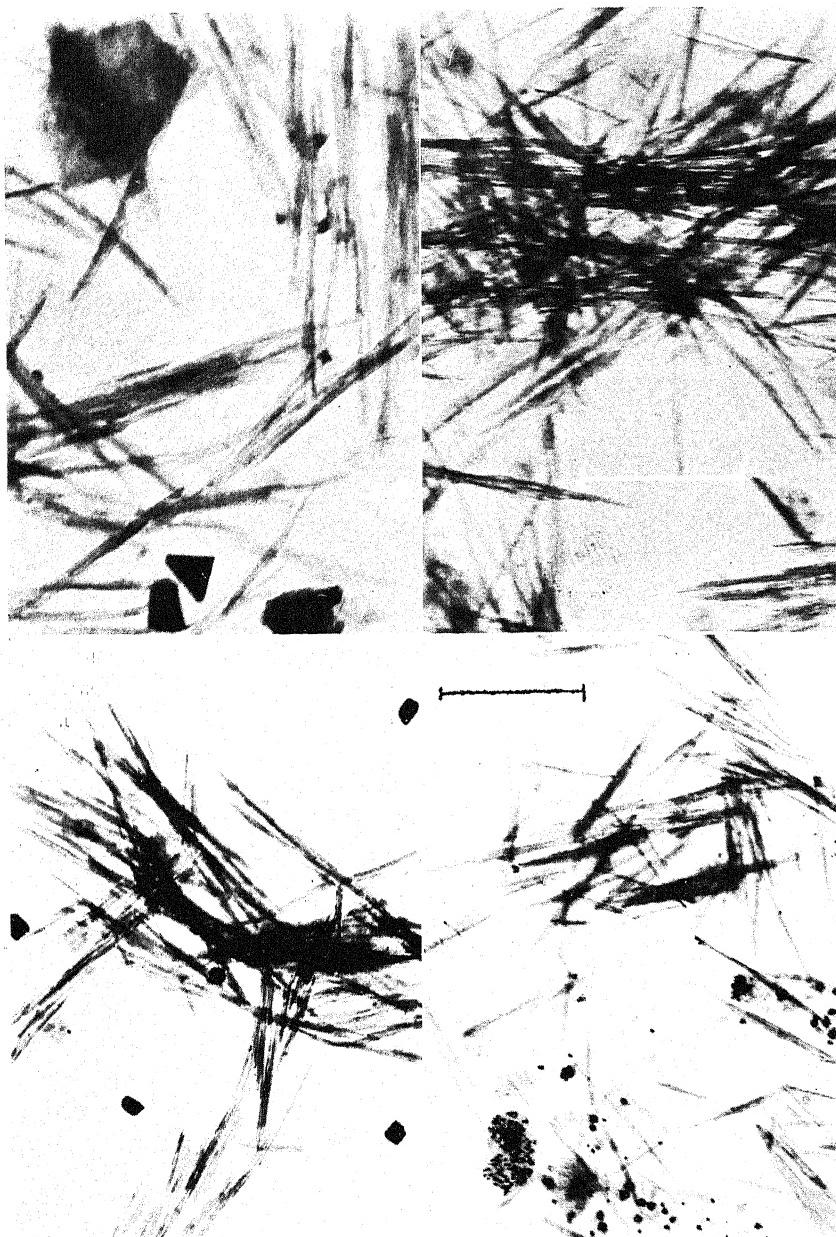
Fig. 9. (upper left) ATTAPULGITE FRACTION 2 μ–500 mμ IN EQUIVALENT
SPHERICAL DIAMETER
Fig. 10. (upper right) ATTAPULGITE FRACTION 500–200 mμ IN EQUIVALENT
SPHERICAL DIAMETER
Fig. 11. (lower left) ATTAPULGITE FRACTION 200–50 mμ IN EQUIVALENT
SPHERICAL DIAMETER
Fig. 12. (lower right) ATTAPULGITE FRACTION < 50 mμ IN EQUIVALENT
SPHERICAL DIAMETER

electron micrographs shown. A particle appearing black, indicating opaqueness to electrons, in these two fractions would have been black in all other reproductions. It is reasonable to assume that the thickness of the mineral grains of the impurity is no greater than their breadth. It is therefore apparent that a particle of this material thicker than 15 mμ is opaque to electrons at the intensity used. It is known that the absorption and scattering of electrons vary with different materials. To be entirely on the safe side it will be granted that absorption and scattering by this material may be 100 per cent greater than in the case of the clay minerals shown. It follows that any particle in any figure not black is less than 30 mμ thick. When two particles overlap and the composite is not black the thickness of the individuals is less than 15 mμ; for three particles the thickness would be less than 10 mμ. Errors in estimation of thickness by densitometer methods, arising from variations in the supporting film, become increasingly important as the thickness of particles approaches or becomes less than the thickness of the nicrocellulose film. Though it is apparent that accurate measurements of thickness are not as yet achieved, the conclusion seems warranted that the plates of beidellite and other clay minerals may be even thinner than considerations of settling velocity would lead one to expect.

<center>DISCUSSION</center>

The use of the electron microscope throws considerable light on the meaning of mechanical analysis within the clay fraction (below 2μ). In some cases, notably Putnam clay (a beidellite), fractionation down to very small sizes appears to have real meaning. The larger particles do not appear to be orientated aggregates of small particles, and their compact character suggests that considerable shearing force would have to be employed within the suspension in order to break them down. The nontronite and magnesium bentonite contained a predominance of aggregates in the coarser fractions, and if complete dispersion had been effected most of the material would have fallen in the finer fractions. In these cases therefore, slight variation in the method of dispersion might cause notable changes in the mechanical analysis figures. Attapulgite represents an extreme example of this tendency, since the finer particles result entirely from cleavage of larger units.

The crystal habit of these clay minerals, here clearly visible for the first time, is in some ways surprising. It was known from ordinary microscopic examination that beidellite was platy and that nontronite formed blades or laths. Nothing was known regarding magnesium bentonite, which is seen to resemble nontronite but to show a greater elongation. Attapulgite was known to be fibrous, but the extreme character of this development was not suspected. Nagelschmidt's suggestion (6) that fibrous or lath-like clay minerals are much commoner than had previously been supposed received confirmation. The lath-like character of nontronite and magnesium bentonite could not be predicted from the general structure ascribed to the montmorillonite group. Some refinements of this general structural type would seem to be foreshadowed.

The extremely fibrous character of attapulgite is in line with the structure proposed for this mineral by Bradley (1).

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DEPENDENCE OF THE RATE OF CORROSION OF BURIED IRON ON THE OXYGEN SUPPLY OF THE SOIL

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Underground corrosion of metals, especially in pipe lines, has been the subject of much research in recent years. The results of the experiments described in this paper, the purpose of which was to determine whether measurements of the rate of corrosion of pieces of iron inserted into the soil might indicate the oxygen-supplying ability of the soil, may be of interest as a contribution to this general topic.

The corrosion of iron is a galvanic process. At anodic points on the surface, metallic atoms pass into solution in the adjacent liquid layer (whether this be only a film of condensed moisture or the interface with a solution), forming positive ions. A variety of reactions may occur at cathodic points, involving the passage of electrons into the solution. The weight of metal dissolving is determined by the quantity of electricity passing (e.m.f. multiplied by time divided by resistance). As in any galvanic cell, the e.m.f. may be regarded as the resultant of separate differences of potential at the anode and at the cathode. In the presence of sufficient moisture, the potential difference at the cathode is likely to be more important in controlling the rate of corrosion of iron in the soil than either the conductivity or the potential difference at the anode.

In general, one or both of two reactions, contributing independently to the flow of current, occur at cathodic points: the liberation of hydrogen gas, and the production of hydroxyl ions from molecular oxygen, thus:

(a) $$2H^+ + 2e^- \rightarrow H_2$$

(b) $$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$

In corrosion by soils, additional cathode reactions are likely to occur involving the reduction of oxidized substances, e.g., ferric ions:

(c) $$Fe^{+++} + e^- \rightarrow Fe^{++}.$$

No direct evidence has yet been published as to the relative importance of the different cathode reactions that are possible in the corrosion of iron in the soil. But the cathode potential difference is controlled by the concentration or rate of supply of reagent at the cathodic areas—hydrogen ions in (a), oxygen molecules in (b), and ferric ions (or other reducible substance) in (c). Clearly, therefore, it would be of practical value to know which of these reagents is most important, or in what circumstances each becomes important. Reaction (b) should pre-

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[1] This study was carried out in the chemistry department of The Imperial College of Tropical Agriculture, Trinidad, B.W.I., during the tenure of a Colonial Agricultural Scholarship.

dominate if conclusions regarding the oxygen supply are to be drawn from corrosion measurements.

The rate of corrosion of iron in distilled water is proportional to the partial pressure of oxygen (14). In pure potassium chloride solutions also it is approximately proportional to the rate of supply of oxygen, but evolution of hydrogen occurs to some extent also, causing departures from exact proportionality (3). Corrosion of iron by water adjusted to different pH values can be divided into three zones with rather indefinite boundaries (15): when the pH is below 4.3 in the case of hydrochloric acid or 5.4 in that of carbonic acid, hydrogen evolution predominates and the rate of corrosion increases rapidly as the pH decreases; at higher pH values up to approximately 10, the rate is nearly independent of pH and is controlled by the oxygen supply; at pH values above 10 the rate decreases, because of the formation of protective oxide coatings (1).

The work of the National Bureau of Standards on the corrosion of buried iron early showed that the rate of corrosion varied to a much greater extent among different soils than among different kinds of iron-pipe materials (9). Many attempts have been made to correlate corrosiveness with other soil properties, notably acidity and conductivity, but it has been noted in a recent summary (10) that several factors appear to be responsible for corrosiveness in soils and that it is improbable that a single satisfactory method for determining corrosiveness can be developed. Several authors who have drawn attention to the importance of aeration have found corrosion to be more rapid in moist than in saturated samples of soil (2, 4, 9, 11, 12, 13, 16, 17, 18). On the other hand, Denison (5, 7) and Denison and Ewing (6) have associated impeded aeration with high corrosiveness, and access of oxygen with comparative freedom from corrosion. The corrosion of pipe lines is complicated by the fact that rather strong currents may flow between anodic and cathodic portions occurring in different types of soil (9), and this may be the cause of apparent contradictions.

FIELD EXPERIMENTS

Strips of commercial mild steel 1 inch wide and $\frac{1}{8}$ inch thick were used in these experiments. For field measurements, these were cut into 6-inch lengths, pointed at one end, bored through with a $\frac{3}{8}$-inch drill near the other, stamped with serial numbers, cleaned of mill-scale with dilute HCl, thoroughly washed with water, dried in a desiccator, and weighed accurately. The average weight was 90 gm. The spikes used in the top 4 inches of the soil were merely coated with wax or varnish for 2 inches at the unpointed end, and pushed straight into the soil up to this coating. The spikes used at greater depths were inserted into slots in the ends of wooden handles (suitable lengths of broom handles), and each was secured with a single wooden peg passing through the hole in the spike and a corresponding hole through the wooden handle. The handles were bevelled on each side of the slot, making them wedge-shaped. The complete instruments therefore resembled spears. In order that the corroding surface should be of the same area in each case, the 2-inch portion of the spike that was inserted in the wooden handle was coated with wax or varnish.

The complete "spears" were driven steadily into the soil with a mallet; if the depth exceeded 1 foot, a hole was made with an auger, slightly less in diameter than the wooden handles, for a part of the required distance. Noticeable disturbance of the soil was avoided, and no gap was allowed to develop between the soil and the handle. Difficulties might have arisen if the soil had been dry and hard, but in those circumstances the water and not the oxygen supply would have been likely to control the rate of corrosion, and the proposed means of studying soil aeration would not have been applicable.

After a designated time the spikes were removed, freed of most of the adhering soil, and placed in dilute NaOH solution for transport to the laboratory. The amount of corrosion was estimated by cleaning the surface and reweighing the spike. It was obviously impossible to determine the weight of the products of corrosion, which became intimately mixed with the soil. The procedure of cathodic treatment in sodium cyanide solution (8) was adopted, in conjunction with light rubbing and scraping. This resulted in a clean and bright surface. The same spikes were used more than once, being kept in a desiccator during intervening periods.

First experiment

The first experiment was carried out during September and the beginning of October, 1939, in the wettest part of Trinidad's rainy season. Six sites were chosen in cacao fields on different types of soil, and measurements of the amount of corrosion occurring in 6 weeks were made on the exposed surfaces of the spikes at four depths at each site: 0–4, 4–8, 8–12, and 24–28 inches. The measurements were made in triplicate. Thus there were 12 spikes at each site. These were inserted in a random fashion in one small block approximately 2 yards square.

The actual losses in weight of the individual spikes and the mean values for the groups of three are shown in table 1.

The features of the six sites may be summarized as follows:

River Estate, Diego Martin Valley.—Level cacao field on uniform compact sandy loam; moderate fertility.

Torrecilla Estate, Arima.—Relatively fertile sandy soil, crumbly in the first 4 inches and then becoming more compact; gravelly below about 2 feet.

Ortinola Estate, Maracas Valley.—Site on a steep hillside, between scattered boulders; porous, crumbly, dark-brown soil, mixed with stones, to a depth of 2 or 3 feet; productivity of cacao very high.

Las Hermanas Estate, San Rafael.—Impervious type of soil; humic surface layer, approximately 1 inch deep, on yellow clay (to 6-inch depth), yellow-and-blue-mottled clay (to 20-inch depth), and blue clay (below 20 inches); surface irregular, because of spreading of lumps of clay thrown up from drains; productivity low.

L'Agnesia Estate, Cumuto.—Site on a gentle slope; impervious type of soil; sandy surface layer approximately 4 inches deep, on sandy clay, yellowish down to the 12-inch depth and then becoming blue with bright-red speckling and mottling.

San Louis Estate, Guaico.—Site in a very wet, low-lying field, of low productivity; clay, almost saturated with water, yellowish down to approximately 15 inches, then yellow-and-blue-mottled.

Soil samples were collected and the following measurements were made: the pH of an aqueous suspension, in the proportion of 3 parts of water to 1 part of

TABLE 1

Losses in weight by corrosion of iron spikes buried for 6 weeks in Trinidad soils at different depths—experiment 1

DEPTH	LOSS IN WEIGHT		DEPTH	LOSS IN WEIGHT	
	Single values	Mean values		Single values	Mean values
inches	mgm.	mgm.	inches	mgm.	mgm.
River Estate			Las Hermanas Estate		
0–4	472 626 ...	549.00	0–4	733 806 908	815.67
4–8	409 541 544	498.00	4–8	885 365 701	650.33
8–12	343 421 334	366.00	8–12	83 202 303	196.00
24–28	124 203 134	153.67	24–28	134 93 211	146.00
Torrecilla Estate			L'Agnesia Estate		
0–4	527 729 794	683.33	0–4	462 272 669	467.67
4–8	535 489 496	506.67	4–8	800 420 452	557.33
8–12	138 521 263	307.33	8–12	259 186 263	236.00
24–28	185 198 120	167.67	24–28	124 188 185	165.67
Ortinola Estate			San Louis Estate		
0–4	720 560 468	582.67	0–4	249 479 369	365.67
4–8	350 465 474	429.67	4–8	239 335 227	267.00
8–12	417 697 580	564.67	8–12	372 182 323	292.33
24–28	281 243 476	333.33	24–28	144 201 178	174.33

fresh moist soil; the percentage of coarse and fine sand together; and the index of texture, which is the percentage of moisture at the sticky point minus one fifth of the percentage of sand. The results are shown in table 2. The electrical conductivities of the suspensions used for pH measurements were also measured, but the results are not reported because the proportions of water and dry soil were not accurately known. None of the values were sufficiently high to indicate the presence of salts such as gypsum, calcium carbonate, or sodium chloride (the extreme range was from 15×10^{-6} to 60×10^{-6} ohms^{-1} per cc.).

Statistical treatment of results. Inspection of the data recorded in table 1 shows that there is much variability within the sets of three values for a particular place

TABLE 2

Analytical data for Trinidad soil samples collected from sites at which iron spikes were buried—experiment 1

DEPTH	pH	SAND	INDEX OF TEXTURE*	pH	SAND	INDEX OF TEXTURE*
inches		per cent			per cent	
		River Estate			Las Hermanas Estate	
0– 4	5.8	42	23	4.4	4	49
4– 8	5.5	44	23	4.7	2	48
8–12	5.7	41	24	4.8	3	48
24–28	5.9	46	20	5.1	3	39
		Torrecilla Estate			L'Agnesia Estate	
0– 4	6.7		9	5.4	44	22
4– 8	6.2	60	14	5.1	39	24
8–12	5.9	(approx.)	11	5.0	21	38
24–28	4.9		16	4.8	23	31
		Ortinola Estate			San Louis Estate	
0– 4	7.1	48	34	4.9	6	47
4– 8	7.1	52	25	4.9	5	49
8–12	6.6	54	17	4.8	6	47
24–28	5.9	55	15	5.1	5	43

* Percentage of moisture at sticky point minus one fifth of the percentage of sand.

and depth, but that there are also large apparent differences between the mean values. Table 3 shows the mean values for the different places (irrespective of depth) and for the different depths (irrespective of place). The significance of these corrosion data was tested by the standard analysis of variance. This analysis is summarized in table 4.

Discussion of results. The analysis of variance proves that there are highly significant differences between the mean values for different depths and between those for different places, and that there is highly significant interaction between places and depths.

The very marked decrease in corrosiveness with increasing depth can be at-

tributed only to a corresponding decrease in the oxygen supply. Moreover, the mean values for sets of three vary from place to place in the same general manner as the oxygen supply may be expected to vary, when the physical properties of the soils are considered. Thus, the amount of corrosion at the 8–12-inch depth was greater at the well-drained site at Ortinola Estate than in the wet and clayey soils at Las Hermanas, L'Agnesia, and San Louis Estates. The low rates of corrosion at the 0–4 and 4–8-inch depths in the San Louis Estate soil are attributable to the water-logged state of this soil, which was particularly noted. Results recorded elsewhere showed that at the time of this experiment the pore spaces of the River Estate soil at the depth of 24–30 inches were almost completely filled

TABLE 3

Mean values for corrosion losses of iron spikes buried for 6 weeks in Trinidad soils— experiment 1

MEAN VALUES FOR DIFFERENT PLACES		MEAN VALUES FOR DIFFERENT DEPTHS	
	mgm.		mgm.
River Estate	391.67	0– 4 inches	577.33
Torrecilla Estate	416.25	4– 8 inches	484.83
Ortinola Estate	477.58	8–12 inches	327.05
Las Hermanas Estate	452.00	24–28 inches	190.11
L'Agnesia Estate	356.67		
San Louis Estate	274.83		
General mean	394.83		394.83

TABLE 4

Analysis of variance: corrosion losses, experiment 1

	VARIANCE	F (BY CALCULATION)	TABLE READING OF F ($P = 0.01$)
Error, means of threes	14,152	....	....
Means of places	63,458	4.48	3.43
Means of depths	527,464	37.3	4.22
Interactions of places and depths	42,781	3.02	2.45

with water; the only site at which aeration might have been better at that depth was at Ortinola Estate. It is therefore notable that the rates of corrosion at that depth were all low and approximately equal, with the exception of that at Ortinola Estate.

It is apparent that there was no general connection between acidity and corrosiveness. Thus, relatively high pH values were recorded for the Ortinola Estate site, and yet the amount of corrosion was also greatest at that site. The exceptionally large amount of corrosion at the two upper depths in the Las Hermanas Estate soil suggested, however, that in this case the high degree of acidity was the controlling factor. A supplementary experiment was therefore carried out at this site, as described later.

Second experiment

The objects of the second experiment were to discover whether the corrosiveness might depend on the weather conditions, to observe whether the initial rate of corrosion of buried iron diminished greatly during 6 weeks (the period used in the former experiment), and to explore the possibility of using the technique that has been described, in measuring the environment of adjacent cacao trees.

The experiment was carried out at River Estate, very close to the site used in the first experiment. In each of four rectangular blocks, A, B, C, and D, measuring 3 feet by 8 feet, were placed 36 iron spikes. Each block covered a heterogeneous patch of ground intersected by one or two filled-in mulch-trenches.

On November 7, 1939, there were inserted in a random fashion in each block 3 iron spikes at a depth of 36–40 inches, 6 at 24–28 inches, and 9 each at 8–12 inches, 4–8 inches, and 0–4 inches. Three spikes were left at each depth for 6 weeks; three, for 4 weeks at each of the 0–4, 4–8, 8–12, and 24–28-inch depths; and the remainder were replaced every 2 weeks over the 6-week period by an equal number of spikes. All the spikes were cleaned and reweighed in the routine manner as soon as possible after removal from the field. Those used in the second and third fortnights were not put into the holes made previously, but were driven in at adjacent spots in the usual way. The data for the losses in weight of the spikes are recorded in tables 5 and 6.

Analysis of results for successive fortnights. The mean values of the corrosion rates for the different fortnights, depths, and blocks are shown in table 7, referring in each case to all the results presented in table 5. The interaction between depths and fortnights is also shown.

The analysis of variance of these results is summarized in table 8.

The time effect. Table 9 shows the difference between the average amount of corrosion of the spikes buried for 4 weeks and that of those buried for the first 2 weeks, for each depth and for each block. This difference was, in general, less than the amount of corrosion of the spikes buried for the second 2 weeks. Similarly, the difference between the values for the 6- and 4-week periods was, in general, less than that for the third 2 weeks. The departures from these generalizations were caused by anomalous individual losses in weight of spikes at the 0–4-inch depth in block A during the 6-week period. The figures obtained by omitting the results for this depth in this block are given at the bottom of table 9; they also come into agreement with the above generalizations.

Analysis of results for 4- and 6-week periods. The mean values for loss in weight at each depth during the longer periods of exposure to corrosion are shown in table 10. The values observed at the adjacent site in the first experiment are also shown. Considerable differences in the 0–4, 4–8, and 8–12-inch depths are apparent. Corrosion was only slightly less, however, at the 24–28-inch depth than at the 8–12-inch depth during the later periods.

Table 11 shows the mean values for loss in weight in each bloc, only the 0–4, 4–8, and 8–12-inch depths being considered. The analysis of variance of the results for these depths in the 4-week period is summarized in table 12. No such

TABLE 5

Losses in weight by corrosion of iron spikes buried for 2 weeks in River Estate soil at different depths—experiment 2

BLOCK	DEPTH	LOSS IN WEIGHT					
		1st Fortnight		2nd Fortnight		3rd Fortnight	
		Single values	Mean values	Single values	Mean values	Single values	Mean values
	inches	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*	*mgm.*
A	0– 4	319 244 219	260.67	222 186 146	184.67	176 174 199	183.00
	4– 8	176 130 216	174.00	170 214 207	197.00	204 152 101	152.33
	8–12	180 124 156	153.33	116 163 335	204.67	165 92 117	124.67
B	0– 4	198 219 166	194.33	177 237 226	213.33	97 134 84	105.00
	4– 8	125 235 215	191.67	215 156 144	171.67	176 143 277	198.67
	8–12	79 126 176	127.00	245 207 268	240.00	117 242 110	156.33
C	0–4	206 212 212	210.00	206 193 228	209.00	139 132 130	133.67
	4– 8	208 193 202	201.00	199 239 215	217.67	189 111 156	152.00
	8–12	237 179 108	174.67	251 165 218	211.33	98 113 111	107.33
D	0– 4	165 151 236	184.00	191 146 165	167.33	113 156 120	129.67
	4– 8	110 118 153	127.00	135 133 109	125.67	121 199 135	151.67
	8–12	136 113 80	109.67	120 156 193	156.33	139 120 84	114.33

TABLE 6

Losses in weight by corrosion of iron spikes buried for 4 and 6 weeks in River Estate soil at different depths—experiment 2

DEPTHS	LOSS IN WEIGHT				LOSS IN WEIGHT			
	4 weeks		6 weeks		4 weeks		6 weeks	
	Single values	Mean values	Single values	Mean values	Single values	Mean values	Single values	Mean values
inches	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
	Block A				*Block C*			
0- 4	654 450 377	493.67	985 957 764	902.00	504 331 357	397.33	355 531 482	459.33
4- 8	293 294 326	304.33	292 470 403	388.33	227 368 431	342.00	391 311 455	385.67
8-12	191 249 216	218.67	193 210 570	324.33	322 291 298	303.67	260 369 460	363.00
24-28	158 185 147	163.33	157 517 162	278.67	402 360 335	365.67	445 381 341	389.00
36-40	... ...	......	142 179 112	144.33	... ...	......	205 230 275	236.67
	Block B				*Block D*			
0- 4	399 414 394	402.33	395 459 533	462.33	300 422 341	354.33	375 386 659	473.33
4- 8	248 358 291	299.00	465 620 378	487.67	265 177 244	228.67	347 551 280	392.67
8-12	207 264 258	243.00	422 284 385	363.67	252 239 197	229.33	249 273 307	276.33
24-28	340 182 202	241.33	301 322 417	346.67	216 177 196	196.33	251 317 207	258.33
36-40	... ...	......	532 392 296	306.67	... ...	......	370 377 427	391.33

analysis of the results for the 6-week period is given, because of the anomalous values at the 0–4-inch depth in block A, referred to above.

Discussion of results. The analysis of variance summarized in table 8 proves that the differences between the average amounts of corrosion in the three successive fortnights were highly significant statistically. Corrosion was greatest in

TABLE 7

Mean values for corrosion losses of iron spikes buried for successive fortnights in River Estate soil—experiment 2

All values in mgm.

Mean values for fortnights		
1st Fortnight	*2nd Fortnight*	*3rd Fortnight*
175.61	191.56	142.39

Mean values for depths		
0–4 inches	*4–8 inches*	*8–12 inches*
181.22	171.67	156.64

Mean values for blocks			
Block A	*Block B*	*Block C*	*Block D*
181.59	177.56	179.63	140.63

Interaction between depths and fortnights

	0–4 inches	*4–8 inches*	*8–12 inches*
1st Fortnight.........................	212.25	173.42	141.17
2nd Fortnight........................	193.58	177.92	203.08
3rd Fortnight.........................	137.84	163.67	125.67
General mean..			169.85

TABLE 8

Analysis of variance: corrosion losses for three fortnights, experiment 2

	VARIANCE	F (BY CALCULATION)	TABLE READING OF F	
			P = 0.05	P = 0.01
Error, means of threes............................	1,737	....	....	....
Means of fortnights................................	22,654	13.04	....	4.93
Means of depths....................................	5,528	3.18	3.13	....
Means of blocks....................................	10,321	5.94	....	4.08
Interactions:				
Depths and fortnights.............................	8,053	4.62	....	3.60
Blocks and fortnights.............................	2,543	1.47	2.23	....
Blocks and depths.................................	1,732	1.00	2.23	....
Depths, blocks, and fortnights...................	1,670	0.96	1.90	....

the second fortnight (November 21 to December 5, 1939), less in the first fortnight (November 7 to 21), and least in the third fortnight (December 5 to 19). The average amount of corrosion at the 0–4-inch depth was greater than that at the 4–8-inch depth, which in turn was greater than that at the 8–12-inch depth; the differences were not large, but they are shown to be significant. There was a high degree of significance in the interaction between depths and fortnights.

These conclusions enable translation of the numerical results summarized in table 7 into the following general terms: In the first fortnight the average rate of corrosion was high between 0 and 4 inches, medium between 4 and 8 inches, and

TABLE 9

Comparison of average corrosion losses of iron spikes buried for 2, 4, and 6 weeks in River Estate soil—experiment 2

	CORROSION IN SECOND 2 WEEKS		CORROSION IN THIRD 2 WEEKS	
	Spikes having corroded for previous 2 weeks	Clean spikes	Spikes having corroded for previous 4 weeks	Clean spikes
	mgm.	*mgm.*	*mgm.*	*mgm.*
All results included				
0–4-inch depth........................	199.67	193.58	162.33	137.84
4–8-inch depth........................	120.08	177.92	120.09	163.67
8–12-inch depth.......................	107.50	203.08	83.17	125.67
Block A.............................	142.89	195.44	199.33	153.33
Block B.............................	143.78	208.33	123.11	153.33
Block C.............................	152.45	212.67	55.00	131.00
Block D.............................	130.56	149.78	110.00	131.89
Mean of all blocks or depths..........	142.42	191.56	121.86	142.39
Results for 0–4-inch depth in block A omitted				
0–4-inch depth.......................	188.55	196.55	80.34	122.78
Block A.............................	97.83	200.84	94.83	138.50
Mean of all blocks or depths..........	131.16	192.91	95.74	138.68

TABLE 10

Mean values for loss in weight by corrosion of iron spikes buried for different periods in River Estate soil at different depths

DEPTH	LOSS IN WEIGHT		
	4 weeks, November 7 to December 5, 1939	6 weeks, November 7 to December 19, 1939	6 weeks, August 29 to October 10, 1939
inches	*mgm.*	*mgm.*	*mgm.*
0– 4	411.92	574.25	549.00
4– 8	293.50	413.59	498.00
8–12	248.67	331.84	366.00
24–28	241.67	318.17	146.00
36–40	......	269.75	......

relatively low between 8 and 12 inches. In the second fortnight it was high at all three depths. In the third fortnight it was medium between 4 and 8 inches, but relatively low between 0 and 4 inches and between 8 and 12 inches. These results are understandable if the oxygen supply is regarded as the controlling

factor, because conditions were fairly wet during the first fortnight, drier during the second, and very wet during most of the third.

The analysis of variance (table 8) also indicates highly significant variation between the blocks, but no significant interaction between blocks and depths or fortnights. The mean values for blocks A, B, and C were practically equal, but that for block D was considerably less than the others. This difference occurred at each depth and in each fortnight (but less markedly in the third fortnight than in the first and second). Block D was actually close to a road at the edge of the field, and it is possible that the soil was less well aerated in it than in the other blocks, because of the run-off of water from the road, or because of less cultivation (in the process of trench-mulching).

TABLE 11

Mean values for loss in weight by corrosion of iron spikes buried for 4 and 6 weeks in River Estate soil at depths of 0–4, 4–8, and 8–12 inches

| BLOCK | LOSS IN WEIGHT | |
	4 weeks, November 7 to December 5, 1939	6 weeks, November 7 to December 19, 1939
	mgm.	mgm.
A	338.89	538.22
B	314.78	437.89
C	347.67	402.67
D	270.78	380.78

TABLE 12

Analysis of variance: corrosion losses during 4 weeks

| | VARIANCE | F (BY CALCULATION) | TABLE READING OF F | |
			P = 0.01	P = 0.05
Error, means of threes...............	4,387	....	....	....
Means of blocks.....................	10,672	2.43	....	2.87
Means of depths.....................	85,366	19.5	5.27	....
Interactions of blocks and depths	5,333	1.22	....	2.37

The results for the 4-week period (November 7 to December 5) agreed with those for the separate fortnights. The analysis of variance summarized in table 12 shows a high degree of significance in the variation between depths. The variation between blocks fails by a fairly small margin to be significant at the 5 per cent level of probability. As before, the amount of corrosion was greatest at the 0–4-inch depth, less at the 4–8-inch depth, and least at the 8–12-inch depth, and was less in block D than in the other blocks.

The amount of corrosion was considerably greater at both the 24–28-inch and the 36–40-inch depths during the 6 weeks of November 7 to December 19 than it was at the 24–28-inch depth between August 29 and October 10. This is attributable to a greater supply of oxygen during the later period than during the earlier, because the conditions were, on the whole, drier.

The comparison of the results for the 2-, 4-, and 6-week periods proves that in soil conditions similar to those encountered during this experiment the rate of corrosion of fresh pieces of iron is greater than that of pieces that have already been in contact with the soil for 2 or more weeks. But as the rate of corrosion does not decrease very abruptly, it seems justifiable to regard the total loss in weight during 2 or more weeks as a measure of the rate of corrosion.

The fact that a significant difference was found between the blocks might suggest that differences in the supply of oxygen to the roots of adjacent trees could be measured by such a method as that under discussion. General observations showed, however, that the soil occupied by each tree at the site of this experiment was very nonuniform. It would actually be preferable to compare blocks of trees on distinct soils in attempting to correlate growth and yield with aeration.

Supplementary experiment at Las Hermanas Estate

It has been noted that there was no general correlation between soil acidity and corrosion in the first field experiment, but that the very high rates of corrosion in the surface layers of soil at the Las Hermanas Estate site might have been attributable to the low pH values observed in that soil (4.4 and 4.7 in the top and second 4 inches respectively). Whitman, Russell, and Altieri (15) found that the rate of corrosion of iron by natural waters was independent of pH between values of 10 and approximately 4.3, but that below 4.3 the rate of corrosion increased rapidly and hydrogen was evolved. The point at which rapid evolution of hydrogen commences depends on the nature of the acid. Thus the difference in pH between the surface soil at Las Hermanas and at the other sites might have been responsible for a change-over to a more intense form of corrosion in the former.

In the first field experiment the losses in weight of all three spikes at 0–4 inches at Las Hermanas were high. Two of the values at 4–8 inches were high, but the third was low, possibly indicating that the pH might be variable at that depth, being nearer to that of the 0–4-inch layer in the burial spots of two of the spikes, and nearer to that of the 8–12-inch layer in the burial spot of the other spike, for all the losses in weight at 8–12 inches were low. On the other hand, the high values at this site might have been caused by the accidental insertion of the spikes at places where the air supply was exceptional, for example, in pockets of crumbly soil mixed with organic residues.

The measurements of corrosiveness were therefore repeated at this site, care being taken to put the upper set of spikes in natural surface soil. The experiment was carried out between the beginning of December, 1939, and the middle of the next month. During this period conditions were much drier, on the whole, than at the time of the first experiment. Four spikes were used at each depth; the time, as before, was 6 weeks. The results are given in table 13.

Soil samples for further pH determinations were collected at the end of the experiment, and close agreement with the previous measurements was found at the three lower depths, but not in the surface layer. A sample of the crumbly humic soil forming a layer approximately 1 inch deep in patches on the surface was found to have a pH value of 5.84, whereas samples of the top 4 inches, not con-

sisting of clay thrown up from the drains, and representing the material in which the upper set of spikes had been placed in this experiment, gave values of 5.06, 5.24, 5.28, and 5.46, as compared with the former value of 4.4. It is evident that the surface soil at this site was irregular, and therefore the second experiment cannot be regarded as a check on the first, although the blocks used for setting out the spikes were only about 3 yards apart.

The individual losses in weight at the 0–4-inch depth were all markedly lower than those found in the first experiment at this site.   This difference may have been the result of the difference in pH, accidental placing of the spikes in unrepresentative spots in the first experiment, or even a comparative lack of mois-

TABLE 13

Loss in weight by corrosion of iron spikes buried for 6 weeks in soil at Las Hermanas Estate—supplementary experiment

| DEPTH | LOSS IN WEIGHT | |
	Single values	Mean values
inches	*mgm.*	*mgm.*
0– 4	564 584 532 554	558.50
4– 8	1011 393 468 346	554.50
8–12	186 440 734 287	411.75
24–28	221 183 164 157	181.25

ture during the second.   The result is not contrary to the view that the acidity is of minor importance in determining the corrosiveness of soil in the field in wet conditions, when the pH is not less than 4.8.   There was one exceptionally high value at each of the 4–8 and 8–12-inch depths, which may have been caused by patches of soil of exceptionally high acidity.

OBSERVATIONS ON OXYGEN ABSORPTION AND HYDROGEN EVOLUTION

The alternative cathodic processes of oxygen absorption and hydrogen evolution have already been discussed.   It appears at first sight to be very simple to carry out laboratory experiments on the relative importance of these two proc-

esses, by placing iron strips in moist soil in closed vessels and analyzing the enclosed air after corrosion has proceeded for a while. The respiration of surface soils is so rapid, however, that it would be necessary in most cases to have means of adding oxygen and absorbing carbon dioxide continually during the experiment. This difficulty was avoided in the experiment described here, by using a clay subsurface soil from which almost all traces of decomposing rootlets were removed. This was mixed with quartz sand, and separate portions were stirred with water, with a 0.018 N solution of $Ca(OH)_2$, and with a 0.036 N solution respectively. After evaporation to a moisture content of 30 per cent, each mixture was broken into crumbs and packed into glass bottles having a capacity of 475 cc., the weight of soil in each bottle being 540 gm. (on an oven-dry basis), that of water 150 gm., and the volume of air approximately 125 cc. Four bottles

TABLE 14

Gas analyses and losses in weight of iron spikes embedded in soil-sand mixtures

NUMBER OF BOTTLE	pH	LOSS IN WEIGHT OF IRON	COMPOSITION OF GAS AFTER 6–8 DAYS			
			CO_2	O_2	H_2	N_2
		mgm.	*per cent*	*per cent*	*per cent*	*per cent*
1	4.6	130	2.42	0.14	7.04	90.40
2	4.6	130	2.16	0.05	3.38	94.41
3	4.6	blank	6.14	11.36	0.00	82.50
4	4.6	blank	5.63	13.21	0.00	81.16
5	5.3	110	1.10	0.00	3.75	95.15
6	5.3	106	0.93	0.00	0.60	98.47
7	5.3	blank	3.94	14.87	0.00	81.19
8	5.3	blank	3.47	17.30	0.00	79.23
9	6.3	94	0.83	0.00	0.86	98.31
10	6.3	125	1.14	0.07	0.00	98.79
11	6.3	blank	1.20	12.90	0.00	85.90
12	6.3	blank	1.24	11.86	0.00	86.90

were packed with each of the three soils; two of the bottles were regarded as "blanks," and weighed iron spikes were completely embedded in the other two. The bottles were fitted with air-tight rubber stoppers bearing narrow manometer tubes containing mercury.

The differences in level of the mercury columns in the arms of the manometers were measured daily. Fluctuations in atmospheric pressure and temperature at the time of measurement were found to be negligible. Between 6 and 8 days after the beginning of the experiment, samples of gas were withdrawn from all the bottles and analyzed with a Haldane apparatus. The iron strips were also cleaned and reweighed. The pH values of the three soils were determined as 4.6, 5.3, and 6.3. The gas analyses and the pressure readings are recorded in tables 14 and 15.

The results show that in the "blanks" slow absorption of oxygen occurred, to-

gether with the production of a smaller amount of carbon dioxide. The bottles that contained spikes showed rapid decreases in pressure, corresponding to the absorption of almost all the oxygen. In some cases this was followed by a gradual increase in pressure, corresponding to the production of hydrogen. The highest concentration of hydrogen was found in bottle 1, which contained soil of pH 4.6; bottles 2 and 5 contained approximately equal amounts of hydrogen, the pH values being 4.6 and 5.3; bottles 6 and 9 contained small amounts of hydro-

TABLE 15

Excess of atmospheric pressure over pressure of enclosed air in bottles containing soil-sand mixtures and embedded iron spikes

In mm. of Hg

NUMBER OF BOTTLE	EXCESS PRESSURE AFTER								
	0 day	1 day	2 days	3 days	4 days	5 days	6 days	7 days	8 days
1	−20	104	134	108	96	84	..	61	..
2	−4	76	71	49	33	15	15	..	..
3	−3	−6	1	8	10	13	..	..	21
4	0	3	2	6	8	10	..	..	15
5	−6	80	100	116	128	129	..	124	..
6	−22	52	70	90	109	125	..	133	..
7	−10	14	19	22	23	24	..	..	29
8	−4	7	11	15	17	17	..	..	21
9	−8	111	134	140	137	134	134	..	..
10	−18	145	148	146	143	141	..	143	..
11	−2	18	27	35	40	43	..	..	58
12	−3	22	29	32	36	35	..	..	44

TABLE 16

Analyses of air in former "blanks" 10 days after insertion of small pieces of iron

NUMBER OF BOTTLE	pH	CO_2	O_2	H_2	N_2
		per cent	per cent	per cent	per cent
3	4.6	1.94	9.40	3.28	85.38
4	4.6	1.75	12.30	4.72	81.23
7	5.3	0.88	18.98	0.62	79.52
8	5.3	1.32	18.92	0.02	79.74
11	6.3	1.24	14.72	0.24	83.80
12	6.3	1.53	15.58	0.05	82.84

gen, the pH values being 5.3 and 6.3; and bottle 10 (pH 6.3) showed no trace of hydrogen.

The average loss in weight, 116 mgm., was equivalent to 23 cc. of oxygen, assuming the product to be in the ferrous state. This was nearly equal to the average volume of oxygen originally in each bottle—21 per cent of 125 cc., or 26 cc.

After the foregoing results had been obtained the "blank" bottles were repeatedly exhausted at the water pump and allowed to fill with atmospheric air.

Smaller pieces of iron than those used previously were then inserted into the soil in each, and the stoppers, with manometers, were replaced. Small decreases in pressure were observed, and after 10 days the analyses of the enclosed air, indicated in table 16, were obtained. These results show much less absorption of oxygen than previously, which may be attributed partly to the smaller surface area of the iron, and partly to the fact that the soil mixtures became somewhat "puddled," thus limiting the rate of diffusion of oxygen. The figures for hydrogen evolution again show a general correlation with acidity.

These data on oxygen absorption and hydrogen evolution are not conclusive, because the experiment was limited to three artificial soil mixtures. They are, however, suggestive of interesting results that might be obtained in a more extensive investigation. It appears that the oxygen-absorption process predominates when the oxygen supply is plentiful, but that hydrogen-evolution may also contribute to the total amount of corrosion, and might alone be responsible for corrosion under anaerobic conditions.

SUMMARY

Strips of iron, attached to wooden handles, were driven into the soil to various depths at several sites in Trinidad, B.W.I., during the rainy season. After 2, 4, or 6 weeks they were removed and cleaned, and the losses in weight determined. The measurements were replicated and the statistical significance of the results was calculated.

Strong evidence of the dependence of the rate of corrosion on the oxygen supply is given by the fact that the loss in weight decreased very markedly with increasing depth, especially during the wettest periods. Except at one site, where pH values of 4.4 and 4.7 in the top and second 4-inch layers of soil may have been the cause of a high degree of corrosiveness, the losses in weight were independent of acidity and were closely related to the oxygen supply, as judged by texture and drainage. None of the soils were saline, calcareous, or gypseous.

Clean iron strips corroded more rapidly than those that had already been in contact with the soil for a fortnight or more.

Three portions of a mixture of sand and clay, virtually free of organic matter, were adjusted to different pH values, and pieces of iron allowed to corrode in each. Manometric observations and gas analyses showed that, of the alternative cathodic processes of oxygen absorption and hydrogen evolution, the former predominated when the oxygen supply was plentiful, but that the latter also played a part, that it might alone be responsible for corrosion in anaerobic conditions, and that its rate increased with acidity.

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ELECTROCHEMICAL RELATIONS BETWEEN THE ROOT SYSTEM AND THE SOIL

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Investigations of the electrical charge of grass roots (especially the roots of wheat), which are surrounded by an aqueous medium, suggested new viewpoints with respect to the properties of the surface layer of the living protoplasm (4, 5, 6, 7). The results of these studies are summarized in this paper.

The surface layer of the protoplasm, called the *Z-layer*, might be characterized as an amphoteric colloid with predominatingly acidic properties. The presence of an acid or a group of acids of high dissociation power (pK probably equals approximately 0.1)[1] entails a comparatively constant H-ion concentration in the Z-layer, if the pH of the medium surrounding the cells is maintained at 3 to 5 and the variation of pH is brought about by solutions of pure mineral acids. If metallic cations are present in the medium, an exchange $M^+ \rightleftharpoons H^+$ (M = metallic cation) occurs, which reduces correspondingly the H-ion concentration of the Z-layer. Besides the acid substances, basic substances are also present in the Z-layer, but in considerably smaller amounts.

A membrane possessing these properties, in contact with a solution containing ions, will exhibit an electrical double layer of opposite signs on both sides of the boundary. The magnitude of the charge can be expressed in terms of H-ion concentrations, according to the formula

$$-\text{P.D.} = \frac{RT}{nF} \ln \frac{[H^+]_z}{[H^+]_o} \qquad (1)$$

where $[H^+]_z$ is the concentration of H ions in the Z-layer and $[H^+]_o$ is the concentration of H ions in the medium. Although the activity coefficients of these ions in the Z-layer and in the medium are unknown, it is believed that because of the low ion concentrations involved the coefficients attain values close to 1. If $[H^+]_o$ is known, the determination of $-\text{P.D.}$ permits of the calculation of $[H^+]_z$. Roots of wheat give a maximal value of about $10^{-3}N$, whereas roots of rye are less acid, about 10^{-4}.

According to formula (1), P.D. can be varied experimentally within the limits of $+10$ and -150 millivolts by varying the cH of the medium. Higher positive charges are excluded because dissociation and $[H^+]_z$ values decrease at high $[H^+]_o$ values. Further, when the acid concentration in the medium exceeds about $10^{-3}N$, the free acid will invade the Z-layer and destroy it. Negative charges above -150 millivolts, on the other hand, are seldom observed, chiefly because of interference of the basic substances in the Z-layer.

Postulating the carriers of the acid and the basic properties of the Z-layer

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[1] Several arguments support the assumption that phosphoric acid radicals, which are linked to some organic compound, are the carriers of the acidity of the Z-layer.

to be nondiffusable through the cellulose membrane (radicals R^- and R^+ respectively), conditions are given for a Donnan equilibrium, according to which the balance between the cations and the anions of a monovalent salt MA is established from the formula

$$\frac{[H^+]_z}{[H^+]_o} = \frac{[M^+]_z}{[M^+]_o} = \frac{[A^-]_o}{[A^-]_z} = \frac{[OH^-]_o}{[OH^-]_z} \qquad (2)$$

where $[M^+]_o$ and $[A^-]_o$ are the concentrations of the ions of the salt MA in the medium, $[M^+]_z$ and $[A^-]_z$ are the concentrations of the same ions in the Z-layer, and $[H^+]_z$ is the *free acidity*.

From our postulate,

$$[H^+]_z + [M^+]_z = [R^-]_z \qquad (2a)$$

and

$$[A^-]_z + [OH^-]_z = [R^+]_z \qquad (2b)$$

In equation (2a) $[H^+]_z$ will be much lower than $[M^+]_z$ even in very dilute solutions; that is, the metallic cations will be strongly adsorbed up to concentrations of about $10^{-2}M$ in the medium. At increasing dilution (5) of the neutral salt MA in the medium, $[A^-]_z$ will accordingly decrease rapidly until $[OH^-]_z$ is approximately equal to $[R^+]_z$. This stage apparently represents a limit which prevents $-P.D.$ from attaining too high values. In the neutral solution of a salt $[OH^-]_o = 10^{-7}$. Assuming $[R^+]_z$ to be about $10^{-5}N$, the limit will be attained when $\frac{[OH^-]_o}{[OH^-]_z} = \frac{10^{-7}}{10^{-5}} = 10^{-2}$. Similarly, if $[R^+]_z = 10^{-4}$, this gives $\frac{[OH^-]_o}{[OH^-]_z} = 10^{-3}$. The highest possible value of P. D. would be -116 millivolts in the first case, and -174 millivolts in the second case. Direct observations of the surface potential of roots in very dilute solutions ($10^{-4}N$ and less) seldom gave higher values than approximately 150 millivolts. The foregoing deduction consequently leads to the conclusion that the concentration of the basic substances in the surface of the protoplasm does not exceed $10^{-5}N$ (due corrections being made for variations in activity coefficients), plus about $\frac{1}{100}$ of the acid substances.

The method previously employed by the author for the determination of P.D. is comparatively simple (4, 5, 7). A detached root 60–80 mm. long is suspended between two solution electrodes. The upper electrode, which encloses the cut end of the root, contains such a high concentration of a salt (e.g., 0.02N KCl) that the P.D. drops to almost zero, as postulated by the Donnan principle. The lower electrode, which encloses the 15–30-mm. tip end of the root, contains acid or salt concentrations, the effects of which on the P.D. are to be tested. By using dilute mineral acids, the $[H^+]_{zmax.}$-value, representing the base-exchange capacity of the surface of the protoplasm of the epidermis cells of the root, can easily be determined. From the observed P.D. values in solutions of neutral salts of varying concentrations, the exchange of cations can be calcu-

lated.   The exchange of cations may be pictured as a chemical reaction between the salt MA and the acid substances R^- of the Z-layer; thus in a monovalent salt

$$HR + MA = MR + HA$$
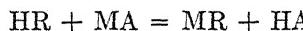
where HR represents the maximum of free acidity of the Z-layer.   By applying the rule of mass action to this formula, the following equation can be developed (7):

$$\log [H^+]_z = \log K - a \cdot \log [MA] \tag{3}$$

This equation has been verified experimentally for a large number of salts with monovalent cations.

The factor a in equation (3) is an expression of the fact that the M ions are accumulated ("adsorbed") on the surface of the root.   This adsorption is related to the Donnan potential: a negative value of P.D. always entails a much higher concentration (activity) of cations in the Z-layer than outside it, in the medium.

Equation (3) is valid for monovalent salts.   For bivalent salts the values of K and a will be changed (7).   This is in accord with the fact that the ions enter the Donnan equilibrium in the reversed rank of their valency ($M^{\frac{1}{n}}$ and $A^{\frac{1}{n}}$). [See also the similar results of Mattson and Wiklander (8) for soil colloids.]

According to formula (3) metallic cations displace H ions from their positions of adsorption (or spheres of attraction, symbolized as R^-).   Similarly, anions (NO_3^-, $H_2PO_4^-$, etc.) are thought to displace OH or HCO_3 ions[2] from the points of negative valency (R^-) in the Z-layer.   Whereas the adsorption of cations decreases P.D., the adsorption of anions will cause P.D. to rise [cOH^- in the Z-layer will fall and consequently cH^+ will rise, according to equations (2) and (1)].   In accordance with this postulate, the different "exchange powers" of homologous ions should be reflected in the P.D.   This is actually the case (6). Because of its higher degree of hydration, the Li ion is adsorbed less strongly and in smaller quantities than is the K ion, and gives higher P.D. values in equimolar solutions.   The Cl ion is adsorbed less strongly and in smaller quantities than the NO_3 ion (10, 11) and, as a consequence, exhibits lower P.D. values. Because of the predominating acidity of the Z-layer, the influence of the cations will always be the limiting factor, and formula (3) consequently represents the approximate reaction of the root system in a solution of a neutral salt.

The Z-layer of a root system is the sum of the surfaces of all epidermal cells, including root hairs.   All solutes taken up by the plant must pass through this thin boundary.   Irrespective of the further mechanism of accumulation of salts (5, 6), the balance of ions in the Z-layer must be a very important factor in the absorption of nutrient ions from the soil.

Ten years ago (3) attention was directed to the apparent similarity between the behavior of the protoplasmic colloids and that of the soil colloids.   The

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[2] Because of respiration, HCO_3 ions are always abundantly present if the pH is not lower than about 5.5 (pK of HCO_3^- is 6.4).

soil is, of course, more heterogeneous than the protoplasm. It consists of a mixture of colloids of acidic and basic properties and reacts generally as an amphoteric colloid with a predominantly acid dissociation, the acid dissociation being increased when large quantities of humus are present (9). If nutrient ions are supplied to the plant by soil colloids instead of by solution, the exchange reactions in the Z-layer are influenced by the cation-adsorptive properties of the soil. A large number of experiments (1) have shown that bivalent-cation (Ca, Mg, Mn) absorption is retarded in the presence of soil colloids when compared with monovalent-cation (K, Na) absorption. Jenny and Overstreet (2) recently ascribed the retarding effect to a contact exchange. But the absorption of nutrients is a gradual process, and it will therefore be necessary also to consider the migration of ions in the soil itself. The transfer of ions from the soil to the Z-layer is retarded by the lowered migration velocity of the ions in the colloidal particles (3). The differences in absorption from the soil of cations of different charge and hydration show a striking parallelism to the transfer of the same ions within the tissues of the plant. Although the movements of monovalent and bivalent ions in an electrical field are not very different when solutions are used, the insertion of a thin colloidal membrane appreciably retards the movement of these ions. The passage of ions through thin colloidal layers in the neighborhood of the surface of the roots will therefore be sufficient, in the course of time, to affect the intensity of absorption.

The electrical potential of the boundary between the roots and the medium reflects at each moment the balance of cations and anions. A series of experiments were conducted in order to elucidate this question.

<div align="center">MATERIALS AND METHODS</div>

Cereals (wheat, rye, oats, and barley) were grown in pots or other vessels containing a soil with a comparatively high percentage of humus (10–20 per cent), but with a low content of nutrients (especially of K, Ca, and N). In some cases the soil was mixed with sand, in order to lower the percentage of humus. Nutrient salts were added at rates corresponding to field applications of fertilizer. The pot experiment was conducted in the summer in a greenhouse at the Institute of Plant Physiology, and the plants showed normal development. Since each pot contained 10–15 plants, it was possible to calculate the mean error of reading by determining P.D. values on 10 plants. All experiments were run in duplicate.

The P.D. determinations were made with a device introduced by the author several years ago, using a cathode-ray oscillograph as a voltmeter and a compensation circuit for calibration. This device is shown diagrammatically in figure 1.

Earlier experience taught (4, 6) that the surface of an organ is virtually discharged at contact with 0.02 N KCl. A comparison between cut roots and intact plants showed, furthermore, that no appreciable P.D. occurs in the longitudinal direction of a root system, if at least 30 mm. of the ends are submerged. It makes only a slight difference if the zero electrode is placed on the cut end

of a single root or at the base of the stalk a few millimeters above the soil. In the present investigation the upper electrode was consistently applied about 1 cm. above the soil, just below the first leaf (fig. 1). The electrode consisted simply of a wad of cotton wool soaked in 0.02 N KCl. Care must be taken, of course, that no drops of KCl run down and cause a short circuit through the soil. A glass tube with KCl-agar serves as a connection with a nonpolarizable electrode (ZnSO$_4$-Hg-Zn), which is connected to the voltmeter.

The second electrode is pushed into the soil. The problem is the determination of P.D. at the boundary between the root system and the soil. For this reason, a possible potential difference between the second electrode and the soil must be eliminated. This was effected by filling a glass tube, 1 cm. in diameter, with cotton soaked in 0.1 N KCl and burying the tube about 1 cm. deep in the soil.
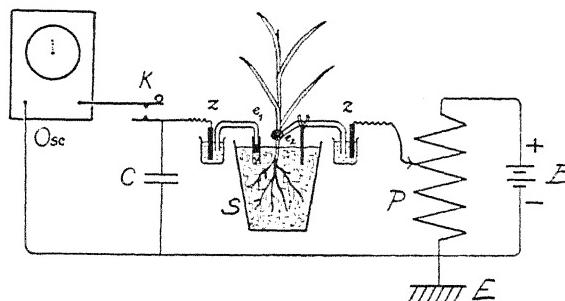
FIG. 1. DEVICE FOR DETERMINING THE POTENTIAL DIFFERENCE BETWEEN THE ROOTS AND THE SOIL

Osc = cathode-ray oscillograph with amplifier; K = telegraph key; C = capacity (20,000 pF); z = Zn-Hg-ZnSO$_4$ electrodes; e_1 and e_2 = KCl-agar terminals; S = top with roots; P = potentiometer in a compensation circuit; B = storage battery for this circuit; E = earth.

The oscillograph is combined with an amplifier, recording a sensitivity of 0.1 millivolt per millimeter deflection. This amplifier works on alternating current. A telegraph key (K in figure 1) serves for the closing and opening of the circuit during the observation, and the capacity C stabilizes the deflections. The whole device is portable.

RESULTS

Three series of experiments were performed: two with the addition of pure salts, and one with the addition of commercial fertilizers.

An interval of 2 to 3 minutes usually must be allowed between the application of the electrodes and the reading, since in the first minute a certain stabilization occurs in the P.D. between the roots and the soil.

A question of some importance is what effect watering has on P.D. In the first series, in addition to the readings made 4 to 7 hours after watering (table 1), other readings were made after an interval of only 1 to 2 hours. Both readings

are plotted in figure 2, and show that, on the whole, the P.D. values determined soon after watering are lower than those determined after an interval of 4 to 7 hours, though the shapes of the curves are similar in both cases.

In the second series (table 2) sodium salts with different anions (Cl^-, NO_3^-, and $H_2PO_4^-$) and nitrates with different cations (K^+, Ca^{++}, Mg^{++}), were compared in equimolar solutions. The individual variation in the observations was sometimes considerable, as in the first series. For this reason conclusions ought to be drawn with due care. Both series (tables 1 and 2) nevertheless show a lower P.D. in the presence of Cl ions than in the presence of NO_3 or H_2PO_4 ions in equimolar solutions. In series 1, the last two anions behave almost identically, whereas in series 2 the NO_3 ion produces a slightly higher P.D. at
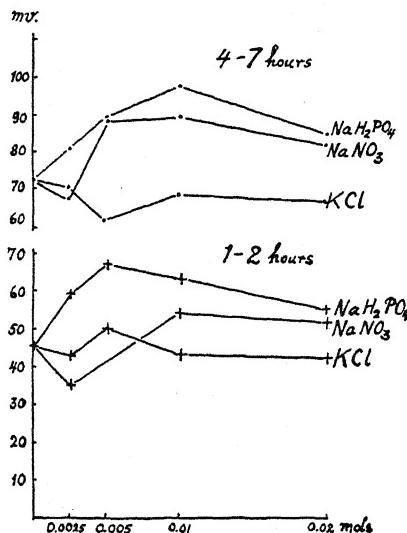
FIG. 2. INFLUENCE OF TIME OF WATERING ON POTENTIAL DIFFERENCE

all concentrations. This difference may perhaps be due to a higher initial content of phosphate in the soil used in series 2.[3]

The influence of the quantity of added NO_3 and H_2PO_4 ions is of a similar order of magnitude in both series, viz., a low P.D. with distilled water, a rise up to 0.005 and 0.01 mol, and then a fall again at 0.02 mol per vessel. The Cl ions produce a more constant P.D. at all concentrations. The series $Cl^- < H_2PO_4$, NO_3^- obtains at all concentrations, except the highest, in series 2.

With respect to the cations, the differences are insignificant at concentrations up to 0.01 mol, but at 0.02 mol concentration the series becomes $K^+ < Ca^{++} < Mg^{++}$.

Table 3 shows the results of some experiments with combinations of KCl and $CaCl_2$. The changes in P.D. are small in comparison to the mean errors, but

[3] This accords with the chemical analyses.

TABLE 1

Effects of additions of varying concentrations of solutions of KCl, NaNO₃, and NaH₂PO₄ on potential difference at the boundary between the root system of wheat and soil mixed with 50 per cent sand

Time of experiment May 21 to June 10, 1941.   Readings taken 4 to 7 hours after watering

SALT CONCENTRATION PER VESSEL	P.D.		
	KCl	NaNO₃	NaH₂PO₄·H₂O
mol	*mv.*	*mv.*	*mv.*
Distilled water only.............	-72.3 ± 5.5	-72.3 ± 5.5	-72.3 ± 5.5
0.0025.........................	-70.5 ± 5.5	-67.7 ± 6.0	-80.8 ± 3.5
0.0050.........................	-62.0 ± 5.0	-88.3 ± 6.2	-89.3 ± 3.3
0.0100.........................	-69.2 ± 4.5	-89.3 ± 5.2	-98.0 ± 3.3
0.0200.........................	-68.3 ± 3.7	-83.0 ± 7.7	-86.2 ± 2.5

TABLE 2

Effects of different anions and cations on potential difference at the boundary between the root system of wheat and soil

Time of experiment June 17 to July 10, 1941.   Readings taken 1 to 2 hours after watering

SALT CONCENTRATION PER VESSEL	P.D.		
	NaNO₃	NaCl	NaH₂PO₄·H₂O
mol	*mv.*	*mv.*	*mv.*
0.0025	-78.6 ± 4.2	-58.4 ± 7.7	-73.4 ± 1.5
0.0050	-86.2 ± 8.2	-70.2 ± 6.4	-83.2 ± 5.3
0.0100	-89.2 ± 5.7	-62.6 ± 1.9	-83.2 ± 5.3
0.0200	-79.6 ± 2.1	-71.0 ± 6.8	-63.8 ± 5.5
	KNO₃	Ca(NO₃)₂·4H₂O	Mg(NO₃)₂·6H₂O
	mv.	*mv.*	*mv.*
0.0025	-63.3 ± 4.0	-74.5 ± 3.0	-67.8 ± 4.3
0.0050	-67.5 ± 6.2	-62.7 ± 5.8	-71.6 ± 6.5
0.0100	-66.5 ± 4.6	-61.2 ± 4.8	-78.6 ± 3.6
0.0200	-53.6 ± 4.5	-65.6 ± 5.0	-78.6 ± 3.6

TABLE 3

Effects of constant KCl and varying CaCl₂ concentrations on potential difference at the boundary between the root system of wheat and soil

Time of experiment June 17 to July 10, 1941.   Readings taken 1 to 2 hours after watering

SALT CONCENTRATION	P.D.
	mv.
0.01 *M* KCl...	-62.2 ± 2.5
0.01 *M* KCl + 0.001 *M* CaCl₂.................................	-69.9 ± 4.9
0.01 *M* KCl + 0.003 *M* CaCl₂.................................	-69.7 ± 2.5
0.01 *M* KCl + 0.010 *M* CaCl₂.................................	-74.9 ± 7.6

a distinct tendency is noticed toward an increase in P.D. with increasing additions of calcium to the potassium salt.

In a third series of experiments, the plants were grown in larger vessels, containing about 25 kgm. of soil of the same type as in series 2. In each vessel, 30 seeds were sown. Commercial fertilizers were added in the usual amounts as single salts or as combinations of salts of the same type as are used in field experiments. The results are shown in table 4.

TABLE 4

Effects of commercial fertilizers on potential differences at the boundaries between the root systems of cereals and soil and on plant yields

Plants grown in Mitscherlich vessels containing soil of the same type as that in series 2. To each vessel of barley, 150 gm. $CaCO_3$ was added

FERTILIZER*	P.D.†			
	Wheat	Rye	Oats	Barley
	mv.	mv.	mv.	mv.
None..............................	77.2 ± 7.5	74.0 ± 7.1	71.1 ± 6.3	64.1 ± 5.3
Potassium salt (2.25 gm. 40 per cent K).	65.6 ± 7.4	45.2 ± 8.4	55.9 ± 5.8	48.0 ± 5.0
Potassium salt + calcium nitrate (4.3 gm.).........................	53.1 ± 6.2	58.3 ± 6.9	55.7 ± 4.7	43.2 ± 2.9
Superphosphate (4.5 gm.).............	84.7 ± 4.7	70.3 ± 5.2	75.0 ± 5.2	54.5 ± 3.9
Superphosphate + calcium nitrate...	57.6 ± 7.4	43.1 ± 6.3	42.7 ± 4.6	44.1 ± 4.6
Superphosphate + calcium nitrate + potassium salt.....................	41.0 ± 5.9	30.0 ± 2.9	44.9 ± 4.8	38.8 ± 2.3

FERTILIZATION	DRY WEIGHT‡			
	Wheat	Rye	Oats	Barley
	gm.	gm.	gm.	gm.
None.............................	0.65	0.34	0.71	0.73
Potassium........................	0.76	0.36	1.03	0.95
Potassium and nitrogen..............	1.63	1.13	2.05	2.02
Phosphate........................	0.80	0.45	0.98	1.12
Phosphate and nitrogen..............	3.17	2.93	4.23	2.97
Phosphate, nitrogen, and potassium...	4.26	3.70	5.98	5.81

* Quantity indicated per vessel.

† Time of experiment August 2 to 22. Readings take ½ to 2 hours after watering.

‡ Per individual plant. Date of harvest, September 26.

Potassium salt (chiefly chloride), on the whole, lowered P.D. even more than did pure KCl in series 1. Superphosphate (chiefly monocalcium phosphate) had no consistent influence on P.D., though on an average, a slight increase was observed. The cation effect ($K^+ < Ca^{++}$) noted in this experiment is similar to that observed in the pure-salt systems.

The combination of nitrogen [as $Ca(NO_3)_2$] and potassium had no consistent effect on P.D., but the addition of nitrogen to phosphate definitely lowered the potential. The drop in P.D. is very considerable for oats and rye. It is dif-

ficult to compare this result with that of the previous series, because the combination of commercial potassium and nitrogen also means a combination of potassium and calcium, whereas the combination of superphosphate and calcium nitrate increases the concentration of free calcium in the soil.

DISCUSSION

The absorption zone of the roots is in close contact with the colloids of the soil (fig. 3). The cellulose wall of the epidermis and root hairs is rather thin ($0.1-3\mu$) but forms, nevertheless, a neutral layer which separates the surface
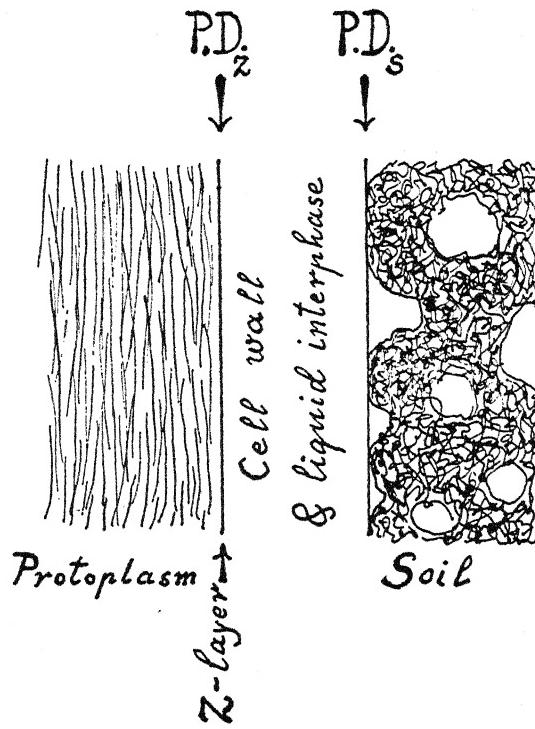
FIG. 3. SCHEME OF THE CONTACT BETWEEN ROOTS AND SOIL

of the protoplasm (Z-layer) from the soil colloids. Nutrient ions which are absorbed by the latter must therefore be detached from the surface of the soil colloids and pass through the aqueous cell walls before they can be absorbed by the living protoplasm. The soil particles seldom form a continuous layer coating the outside of the root hairs, but are irregular, with intervening spaces covered by an *aqueous film* or, after watering, by a film of soil water. The aqueous film between the soil colloids and the absorbing surface of the roots is therefore always a factor in the process of the uptake of mineral nutrients by the plant.

As has been shown, the Z-layer behaves as an amphoteric colloid with pre-

dominantly acidic properties. The free acidity of this layer, $[H^+]_z$, attains its maximum when metallic cations are absent from the medium. In the presence of metallic cations the free acidity decreases rapidly, approximately following formula (3). The points of negative valence (R^-) are consequently normally saturated by a small quantity of H ions (= free acidity) and a larger quantity of M ions (= adsorbed metallic cations). This fact implies that no fundamental difference exists between the uptake of ions from a solution and from a colloid. In the soil the solution is reduced to an aqueous film around the colloid. Exchange reactions occur, on the other hand, between this and the soil colloids. In the natural process of absorption from the soil all stages of transference of ions, from a free solution to adhering colloidal particles, occur. In a dry soil the aqueous film will be reduced to capillary layers of water, and the colloids will be coagulated. In a moist soil the aqueous film will extend to form substantial layers of solution.

In the same way as an electrochemical boundary is developed near the Z-layer, a second boundary develops at the interphase between the aqueous film and the soil colloids (see figure 3). If P.D.$_z$ and P.D.$_s$ are the potential differences at these boundaries,

$$\text{Observed P.D.} = \text{P.D.}_z - \text{P.D.}_s \tag{4}$$

Determination of P.D. now makes possible an estimation of the magnitude of P.D.$_s$.

In isolated roots, as well as in root systems, which are kept in normal nutrient solutions, a potential difference of -50 to -60 millivolts was usually observed (6). Our determinations (tables 1 to 4) gave an average of all the values at moderate fertilization of 62.7 millivolts. If the P.D.$_s$ in a solution is zero, we find from equation (4) that it attains a negligible value also in the soil in question.

Employing the formulas

$$-\text{P.D.}_z = \frac{RT}{nF} \ln \frac{[H^+]_z}{[H^+]_o} \text{ and } -\text{P.D.}_s = \frac{RT}{nF} \ln \frac{[H^+]_s}{[H^+]_o}$$

in which $[H^+]_o$ represents the H-ion concentration of the aqueous film which separates the two boundaries, we get

$$\text{P.D.}_z - \text{P.D.}_s = \frac{RT}{nF} \ln \frac{[H^+]_z}{[H^+]_s} \tag{5}$$

Here $[H^+]_s$ is the free acidity of the soil in the boundary between roots and soil. If P.D.$_s$ is very small $[H^+]_s$ practically equals $[H^+]_o$, which in normal nutrient solutions usually attains a value of about 10^{-6} (the pH of the nutrient solution being 6 to 6.2 for wheat). The normal exchange acidity of the surface of the root system under these circumstances is about $10^{-5} N$. These values are, of course, only approximate.

Since P.D., according to formula (5), is an exponent for a surplus of free acidity of the Z-layer in comparison to the surface of the soil colloids, and the

relations $\frac{[H^+]_z}{[H^+]_o}$ and $\frac{[H^+]_z}{[H^+]_s}$ are an expression of the power of adsorption with respect to the cations, it may be concluded that no appreciable "contrapressure" with respect to cations occurs in our soils.

The results support the concept, previously advanced by the author, that the observed retardation of the uptake of ions of higher charge from a colloidal substrate is due not so much to a direct adsorption competition at the interphases, as to a retarded migration of ions in the colloidal films or masses of particles. The effect of watering also points in this direction. In a dry soil P.D.$_s$ would be expected to attain its maximum. But this is not the case. The soil interphases seem, on the contrary, to be almost exhausted with respect to metallic cations, to the benefit of the Z-layer. The transfer of ions proceeds slowly with lack of water. Watering increases the ion concentration in the aqueous films around the colloids and, as a consequence, more ions are available for absorption by the roots.

In earlier experiments (3), mixtures of pure granulated quartz and small amounts of colloids (humus, SiO_2-gel) were used. The soil used in the present investigation contained much more humus. Further experiments will show whether or not other soils behave differently. It is believed, however, that humus colloids in general have a much lower cation adsorption power than living protoplasm. This observation throws light on the known fact that cereals are capable of absorbing 100 to 1,000 times more potassium and sodium than is the same volume of dry soil.

The prevailing state of adsorption equilibrium is expressed by P.D. Cations and anions are continuously passing from the Z-layer into the root. On the other hand, the close agreement between the magnitudes of P.D. in isolated roots and in intact root systems, in solutions or in soil, shows that the roots are usually not far from an adsorption equilibrium with their surroundings. This conclusion is of interest because appropriate combinations of adsorbed cations seem to condition normal functions of the living protoplasm (6).

The conclusion that the "contrapressure," symbolized by P.D.$_s$, is virtually negligible in the soil used in these experiments simplifies the explanation of the results.

Formula (3) is valid down to concentrations of about 10^{-4} N. At further dilution of the salt, the basic substances of the Z-layer interfere, and P.D. ceases to increase. In the present experiments, the actual concentration of the nutrient ions in the boundary between the roots and the soil is not known but is probably low, in view of the fact that the ions are rapidly absorbed. The soil used was lacking in potassium and sufficient amounts of calcium. Unmanured, the soil will affect the roots much in the same way as a very dilute solution. That P.D. increases after the addition of small amounts (0.0025–0.005 mol) of salts is therefore in accord with previous experiences (6, fig. 5). Increasing amounts of cations above this lower limit will again cause the P.D. to drop. This situation is developed in the soil after the addition of commercial calcium nitrate to superphosphate and further additions of commercial potassium salt: P.D. falls rapidly with this increasing fertilization.

A higher P.D. was developed in the presence of NO_3 ions and H_2PO_4 ions than in the presence of Cl ions. Solutions and soil behave in the same manner. The soil used in the experiments did not contain much calcium, but enough was present to prevent the discharge of the Z-layer. The addition of calcium salt resulted, nevertheless, in a further slight rise of P.D. (table 4). The addition of commercial calcium phosphate (superphosphate) also resulted in a higher P.D. The phosphate ion increases the effect.

The main conclusion to be drawn from this study is the fact that root systems behave in virtually the same manner in the soil as in a solution and that observed differences in respect to the absorption of nutrient ions are due to the special conditions of the transfer of ions within the soil and the mutual exchange of ions between the soil colloids and the aqueous film surrounding the roots. Another problem of general interest is whether P.D. can be used as a criterion of the ability of the soil to furnish the roots with ions.

Because of its pronounced acidity, the surface of the root system attracts cations intensively, resulting in a close relation between P.D. and salt concentration, which is regulated according to formulas (1) and (2). As a consequence, the determination of P.D. aids in the elucidation of the total amount of available salts, but conclusions as to the kind of salts are, of course, impossible. In combination with a partial chemical analysis of the soil, some further information can be gained.

If the chemical analysis of the soil extract shows large amounts of nutrients, P.D. will be low (30–40 millivolts; see table 4) under all circumstances, because a large quantity of cations always keeps down both $P.D._z$ and $P.D._s$. But a low P.D. may also be the result of a high "contrapressure" in the soil colloids, a high $[H_s^+]$, and consequently a low $\dfrac{[H^+]_z}{[H^+]_s}$ [see equations (4) and (5)].

In the soil used, which was rich in humus, the free acidity is about ten times lower than the free acidity of the surface of the roots, resulting in a P.D. of about -60 millivolts. The method advanced in this paper undoubtedly opens up a possibility of investigating the free acidity of different types of soil, because the value $[H^+]_z$ can be determined otherwise. In soils of the same type as that used in the present investigation, a low P.D. always indicates large amounts of available salts.

If, now, the chemical analysis of the soil revealed a low content of nutrients, a comparatively high P.D. ought to be expected (60–70 millivolts), on the assumption that $P.D._s$ is negligible. A low P.D. would, under these circumstances, indicate a comparatively high free acidity of the soil, according to equation (4).

Finally, the determination of P.D. opens up a possibility of further control of fertilizer experiments. Table 4 illustrates a striking inverse relation between P.D., determined only 2 to 3 weeks after germination, and the yield of the ripened plants, after 7 weeks of growth. This relation between P.D. and yield is probably valid only in the presence of sufficient nitrate, because the other nutrient factors, potassium and phosphate, are largely dependent on the nitrogen factor. A low P.D. always favors the absorption of anions, because these are repelled by

a negatively charged root surface. In the presence of sufficient nitrate, a low P.D. always indicates an abundant supply of other nutrients.

SUMMARY

A method is described by means of which the potential differences between the soil and the root system of plants can be determined.

A few equations illustrate a theory of the electrochemical properties of the surface of living roots, which control the absorption of nutrient ions. This theory is also extended to the boundary between the roots and the soil.

A number of determinations of the potential of cereal plants, grown in soil to which nutrient salts or commercial fertilizers were added, are discussed against the background of the theoretical considerations.

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FACTORS AFFECTING THE INTERACTION BETWEEN ORGANIC MATTER AND MONTMORILLONITE[1]

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The beneficial effect of organic matter on the physical properties of soils depends to a considerable extent upon the interaction of the organic and inorganic colloids present. The extent of the interaction between the two colloids depends upon such factors as reaction of the soil and the nature and abundance of the organic matter. The union taking place between the two fractions of the soil is also important from the standpoint of soil-forming processes.

There is a need for more basic information concerning the factors that influence the binding of organic matter by inorganic colloids. This investigation was designed to study in detail such factors as pH, grinding and composting, and various kinds of organic materials.

The data presented by Demolon and Barbier (2), Mattson (7), Meyers (8), Gieseking (5), and Ensminger and Gieseking (3, 4) show that organic substances have a tendency to react with clays. The nature of these reactions has been studied by several investigators. Gieseking (5) found that complex organic cations were strongly absorbed within the variable (001) spacing of montmorillonitic clays, resulting in larger (001) spacings. Ensminger and Gieseking (3, 4) found that gelatin and albumen were absorbed within the expansible portion of montmorillonite, also resulting in larger (001) spacings. Furthermore, the addition of gelatin resulted in a reduction in the base-exchange capacity of montmorillonitic clays, the amount of the reduction depending upon the hydrogen-ion concentration of the mixture. Meyers (8) observed that organic colloids reduced the base-exchange capacity of inorganic colloids. He suggested polar adsorption as the most probable type of reaction.

EXPERIMENTAL TECHNIC

Electrodialyzed Wyoming bentonite ($<0.5\mu$ in diameter) was used in this investigation. The bentonite was predominantly montmorillonite and had a base-exchange capacity of 90 m.e. per 100 gm.

Wheat straw, which had been ground in a Wiley mill, and alfalfa leaf meal were used in order to compare materials of both high and low nitrogenous contents. These two materials and a mixture containing 50 per cent straw and 50 per cent alfalfa leaf meal were composted and samples taken out at various intervals. For the grinding experiments these materials were ground dry in a ball mill for 4 hours at 90 revolutions per minute.

The lignin was prepared by treating wheat straw with 72 per cent sulfuric

[1] Published with the approval of the director of the Idaho Agricultural Experiment Station as Research Paper no. 189.

acid. The lignin was washed with distilled water until free of acid and then was suspended in water. The lignin-gelatin complexes were prepared by mixing slightly alkaline suspensions of lignin and gelatin together and adjusting the acidity to pH 4.0 with HCl.

The organic-inorganic complexes prepared at pH 2.8 were mixed together, and the acidity was adjusted by adding HCl. For higher pH values, suspensions of the materials were made slightly alkaline before mixing and then adjusted to the desired pH by adding HCl.

The base-exchange capacity was determined by saturating with barium. The complexes were leached with a saturating solution of $BaCl_2$ until the pH of the percolate reached a value of about 6.0. The unsorbed barium was removed by leaching with double distilled water until the leachate no longer gave

TABLE 1

Equivalent combining weight of protein cations for montmorillonite

QUANTITY OF PROTEIN ADDED TO 1 GM. OF MONTMORILLONITE	pH	BASE-EXCHANGE CAPACITY OF CLAY	EQUIVALENT COMBINING WEIGHT OF PROTEIN CATIONS FOR MONTMORILLONITE
		m.e./100 gm.	
0.25 gm. gelatin............	7.0	78.0	2083
	5.5	69.0	1190
	4.0	62.0	893
	2.8	55.7	729
	1.5	49.0	610
	1.0	46.0	568
	0.5	43.5	538
0.25 gm. albumen............	7.0	83.0	3571
	5.5	78.5	2173
	4.0	72.5	1429
	2.8	67.5	1111
	1.5	63.0	926
	1.0	62.5	909
	0.5	62.5	909

a test for chloride. The sorbed barium was replaced by leaching with $0.1N$ HCl and the barium determined gravimetrically. Since the exchange capacity of the electrodialyzed montmorillonite was determined in the same manner, any reduction in the exchange capacity of the montmorillonite on the addition of organic material should be attributable to the interaction of the organic material and clay.

RESULTS AND DISCUSSION

Sorption of proteins by montmorillonite

The data in table 1 show that gelatin and albumen reduce the exch nge capacity of montmorillonite, and that the effectiveness of the protein in this respect depends on the pH of the complex. It is interesting to note that the

combining capacity of gelatin increases with acidity over the pH range measured. In the case of albumen the basic properties reach a maximum value somewhere between pH 2.8 and 1.5.

The maximum combining weight of gelatin and albumen for HCl as reported in the literature ranges from 1042 to 1125 for gelatin and 1200 to 1250 for albumen. Gelatin sorbs about as many equivalents of clay at pH 5.5 as it does HCl at any pH measured. Albumen sorbs only about half as many equivalents of clay at pH 5.5 as it does HCl at any pH measured. Since it is difficult to measure acid binding of proteins below pH 2.5, very little is known about their basic properties in this range. According to these data only 12 per cent of the nitrogen in gelatin and 8 per cent of that in albumen are basic at pH 2.8. In most proteins only the amino nitrogen is considered basic. Bancroft and Barnett (1) found, however, that deaminized gelatin had a combining capacity for HCl amounting to 0.0044 gm.-equivalents. They suggested

that the combining capacity of deaminized gelatin is due to the $-\overset{\displaystyle O}{\overset{\displaystyle \parallel}{C}}-N-$ groups, which are not attacked by nitrous acid.

Sorption of straw and alfalfa leaf meal by montmorillonite

The next logical step was to use something that more nearly approaches the type of organic matter found in soils. Finely chopped wheat straw and alfalfa leaf meal were selected for this purpose. These materials, as well as a mixture of the two, were composted in gallon jars. They were kept in a moist state, and enough ammonium phosphate was added to the straw to bring the nitrogen content up to about 1.7 per cent, which is the amount considered necessary for active decomposition. Table 2 gives the base-exchange capacity of the original and the composted material before and after being ground 4 hours in a ball mill.

Base-exchange capacity increased with an increase in time of composting, and the capacity of alfalfa leaf meal was more than twice as great as that of straw in most cases. The capacity of composted straw-alfalfa mixture was only slightly less than that of composted alfalfa leaf meal. Grinding increased the exchange capacity of alfalfa leaf meal, but an increase in composting time lessened this effect. Grinding had little or no effect on the capacity of straw either before or after composting.

The degree of sorption of organic materials before and after composting and grinding was determined by base-exchange measurements. The exchange values for montmorillonite reported in tables 3, 4, and 5 were obtained by determining the capacity of the organic-inorganic mixture and subtracting the capacity of the organic fraction from it. Therefore, the original capacity of montmorillonite, which is 90 m.e., minus the values for montmorillonite in the tables, gives the reduction in capacity due to the organic material added. The data in table 3 show the reduction of exchange capacity of montmorillonite caused by the additions of various organic materials. These figures show that

TABLE 2

Influence of composting and grinding on the base-exchange capacity of organic matter

ORGANIC MATERIAL		BASE-EXCHANGE CAPACITY	
		Unground	Ground 4 hours in ball mill
		m.e./100 gm.	*m.e./100 gm.*
Alfalfa leaf meal		38.5	51.0
Alfalfa leaf meal composted	1 month	81.0	88.0
	3 months	90.5	97.5
	6 months	103.0	107.0
	9 months	110.0	115.0
Wheat straw		12.5	12.5
Wheat straw composted	1 month	27.0	28.5
	3 months	42.0	44.0
	6 months	60.0	62.0
	9 months	62.0	62.0
½ alfalfa + ½ straw		26.0	32.0
½ alfalfa + ½ straw composted	1 month	74.5	79.0
	3 months	83.0	90.0
	6 months	100.0	101.0
	9 months	108.0	112.0

TABLE 3

*Effect of grinding and composting on the sorption of organic matter by montmorillonite**

AMOUNT AND KIND OF ORGANIC MATTER ADDED TO 1 GM. OF MONTMORILLONITE	TIME OF GRINDING IN BALL MILL	BASE-EXCHANGE CAPACITY OF MONTMORIL-LONITE	NITROGEN
	hours	*m.e./100 gm.*	*per cent*
0.5 gm. straw	0	87.3	0.61
	4	86.0	0.61
0.5 gm. straw composted 3 months	0	75.2	2.21
	4	72.8	2.21
0.5 gm. straw composted 6 months	0	70.5	2.51
	4	68.0	2.51
0.5 gm. alfalfa leaf meal	0	73.0	3.27
	4	64.7	3.27
0.5 gm. alfalfa leaf meal composted 3 months	0	61.7	3.32
	4	55.0	3.32
0.5 gm. alfalfa leaf meal composted 6 months	0	50.0	3.60
	4	45.0	3.60
0.5 gm. alfalfa + straw composted 3 months	0	62.0	3.36
	4	56.0	3.36
0.5 gm. alfalfa + straw composted 6 months	0	52.0	3.60
	4	48.0	3.60

* Complexes acidified to pH 2.8.

composting increases the amount of reaction taking place between the organic materials and clay, and that alfalfa is sorbed to a much greater extent than straw. The alfalfa-straw mixture follows rather closely the trend of alfalfa. Grinding has little effect on the sorption of straw but has considerable effect on the sorption of alfalfa and alfalfa composts.

If the sorption is due to basic nitrogen groups, then some of the difference between straw and alfalfa can be explained on the basis of difference in nitrogen

TABLE 4

Influence of pH on the sorption of organic matter by montmorillonite

AMOUNT AND NATURE OF ORGANIC MATTER ADDED TO 1 GM. OF MONTMORILLONITE	pH	BASE-EXCHANGE CAPACITY OF MONTMORILLONITE
		m.e./100 gm.
0.25 gm. gelatin	7.0	78.0
	5.5	69.0
	4.0	62.0
0.25 gm. alfalfa leaf meal	7.0	90.0
	5.5	82.0
	4.0	79.0
0.25 gm. alfalfa leaf meal composted 6 months	7.0	87.8
	5.5	77.4
	4.0	66.0

TABLE 5

Influence of acid-lignin on the sorption of gelatin by montmorillonite at pH 2.8

COMPOSITION OF LIGNOPROTEIN COMPLEX ADDED TO 1 GM. MONTMORILLONITE	BASE-EXCHANGE CAPACITY OF MONTMORILLONITE
	m.e./100 gm.
0.5 gm. gelatin	42.0
0.5 gm. gelatin:0.5 gm. lignin	45.0
0.5 gm. gelatin:1.0 gm. lignin	47.5
0.5 gm. gelatin:2.0 gm. lignin	53.0
0.5 gm. gelatin:3.0 gm. lignin	58.0
0.5 gm. gelatin:4.0 gm. lignin	61.0
0.5 gm. gelatin:5.0 gm. lignin	62.0

content. Since straw is much lower in nitrogen, it probably would have fewer basic nitrogen groups. On the other hand, all of the increased sorption of alfalfa on composting cannot be attributed to an increase in percentage of nitrogen. As previously mentioned, 8–12 per cent of protein nitrogen is basic as measured by sorption, whereas as much as 35 per cent of the nitrogen of alfalfa would have to be basic to account for the reduction in base-exchange capacity of montmorillonite.

The increased sorption of alfalfa on grinding may be due to the fact that more

nitrogen groups are exposed and thereby have a chance to react with the clay. Straw is low in nitrogen, and therefore, grinding has little effect on sorption.

Composting increases the nitrogen content of straw, which may explain the increased sorption on composting. The greater sorption of alfalfa on composting cannot be explained, however, entirely on the basis of nitrogen content. Composting would be expected to result in the hydrolysis of nonbasic peptid groupings, and, as products of these reactions, basic nitrogenous compounds would be formed. Composting also tends to increase the activity of these organic materials in that they are more finely subdivided than the corresponding uncomposted materials.

pH in relation to sorption of organic matter

Since most agricultural soils have a pH above 5.0, it is important to know something about the interaction that might take place at higher pH values. As measured in the laboratory, pH is often higher than under field conditions. Soils in the field produce a certain amount of carbon dioxide, which affects the pH materially. The amount of carbon dioxide produced depends on the activity of the microorganisms, the quantity of organic matter present, and the evolution of gas by roots of living plants. McGeorge and Breazeale (6) believe that the carbon dioxide from roots may reduce the pH of calcareous soils to 6.2 or less within a limited area around the root zone. According to Truog (9) a pH of 4.0 can be closely approached at the root surface. Table 4 shows the effect of acidity on the sorption of gelatin, alfalfa leaf meal, and alfalfa leaf meal composted 6 months. The composted material is much more strongly sorbed at pH 4.0 and 5.5 than the uncomposted material.

Effect of acid-lignin on basicity of gelatin

Soil organic matter is composed largely of lignoprotein complexes. According to Waksman (10), the properties and reactions of soil lignoproteins and lignoproteins synthesized in the laboratory are very similar. The ratio of lignin to protein in soils varies from 3:1 to 0.5:1. Some lignogelatin complexes, therefore, were prepared in the laboratory to determine what effect lignin has on the basic properties of gelatin. It is evident from table 5 that increasing amounts of lignin decreased the sorption of gelatin by montmorillonite. If the NH_2 groups of the gelatin react with the ketonic or aldehydic groups of the lignin to form a Schiff's base type of compound, the nitrogen may lose some of its basic properties, or some of the NH_2 groups may be covered up mechanically so that they cannot react with the clay.

CONCLUSIONS

Factors affecting the interaction of organic materials with montmorillonite have been studied. Such organic materials as gelatin, albumen, straw, alfalfa leaf meal, and lignin were included.

The combining capacity of gelatin increases with acidity, at least to pH 0.5, and the basicity of albumen increases with acidity to a pH value somewhere

between 2.8 and 1.5 and then remains constant. The equivalent combining weight of the gelatin cation is greater for montmorillonite than for hydrochloric acid. The equivalent combining weight of the albumen cation is about the same for montmorillonite and hydrochloric acid. According to the base-exchange data, 12 per cent of the nitrogen in gelatin and 8 per cent of that in albumen are basic at pH 2.8.

Composting increases the base-exchange capacity of straw and alfalfa leaf meal. Grinding increases the capacity of alfalfa leaf meal but has little effect on straw.

Composting increases the sorption of straw and alfalfa leaf meal by montmorillonite. Grinding increases the sorption of alfalfa leaf meal and its composts but has little effect on the sorption of straw. Organic materials containing alfalfa are sorbed to a greater extent than straw. The fact that alfalfa contains more nitrogen than straw may be a partial explanation. About 35 per cent of the nitrogen would have to be basic to account for the reduction in base-exchange capacity of montmorillonite.

Acidity increases the sorption of composted alfalfa leaf meal more than it does the original material.

The addition of lignin to gelatin decreases the basic properties of gelatin.

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SIGNIFICANCE OF DONNAN EQUILIBRIA FOR SOIL COLLOIDAL SYSTEMS

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Received for publication May 11, 1942

Many soil chemists approach the qualitative and quantitative study of their problems from the viewpoint of Donnan equilibria. In particular, the school of Mattson has produced a voluminous literature on the colloidal behavior of the clay and humus fraction of the soil. Base exchange, suspension effects, swelling and shrinking, clay formation, etc., are claimed to be primarily consequences of the Donnan equilibrium. Considerable uncertainty and even confusion, however, exist among soil chemists regarding the fruitfulness of this concept in its application to soil chemistry. If we recall that Donnan's famous contribution appeared over 30 years ago, long before soil chemists began to utilize Lewis' concept of activity and before the advent of the Debye-Hückel theory of electrolytes, it is small wonder that many investigators are skeptical about the validity of the Donnan equilibrium in its original form and in its usual presentation.

It is the purpose of this paper to present the results of a critical reinvestigation of the Donnan equilibrium in relation to clay systems. Emphasis is placed on an exact thermodynamic treatment, as the customary discussion is found to be insufficient. A brief description of Donnan systems and Donnan equilibria is followed by a critical discussion of the thermodynamics of Donnan equilibria based upon the exact thermodynamic treatment by Donnan and Guggenheim. Finally, the application of these principles to ideal and real systems and the significance of Donnan equilibria for soil colloids are considered.

THEORETICAL DISCUSSION OF DONNAN EQUILIBRIA

Donnan systems

Systems of two or more phases,[2] each of which contains a different concentration of colloidal material and which has therefore a measurably different ionic content, may be conveniently called *Donnan systems*. As a simple example, we may take an aqueous suspension containing sodium clay and NaCl which is separated by a membrane from an aqueous solution of NaCl, as indicated in figure 1, where A^- represents the negatively charged clay particles.

In this system only one phase, which we shall call the *colloid phase*, contains an appreciable quantity of colloidal material. The other phase is noncolloid. Donnan systems are not restricted to such simple arrangements. The principles discussed in the following paragraphs can readily be extended to systems of any

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[1] The author is indebted to H. Jenny and R. Overstreet for suggestions and criticism.

[2] The author follows Guggenheim, MacDougall, and Brönsted in using the term "phase" to refer to any homogeneous region in a heterogeneous system. The phases discussed in this paper are generally aqueous solutions or suspensions.

number of phases, each of which may contain colloidal material. Furthermore, the different phases of Donnan systems need not be separated by physical membranes. In principle, any restraint such as gravitational or centrifugal force, which can be utilized to prevent diffusion of particles from one phase to another, may be substituted for the membrane.

The discussion of Donnan systems need not be restricted to arbitrary systems which contain only strong electrolytes and completely dissociated colloids. The concentrations of ionic species to which reference will be made will represent the total replaceable content of such components, not necessarily the content of dissociated ions.

It will be convenient to limit our discussion in one or two respects. Only Donnan systems in which both phases contain the same solvent will be considered. Furthermore, the small osmotic pressure difference between two phases in a clay system will be neglected.

The concepts of Donnan systems and the related Donnan equilibria will be restricted to phases which are so large that measurements may be made upon each phase. These concepts will not be extended to microsystems, such as those formed by the "micellar" and "intermicellar" regions within a suspension, or to the successive infinitesimally thick shells of ions in the ion swarm, double layer, or micellar atmosphere surrounding a colloidal particle.

Although several authors, for example Robinson (25), have discussed equilibria in such systems and have employed the term *Donnan equilibria* in their characterization, this usage does not appear to be desirable. A detailed review and criticism of these attempts is not necessary. There are at least two objections to the application of the Donnan terminology to microsystems: First, whenever a system of more than one phase having measurable dimensions is under consideration, it is confusing to apply the same terms to the relationships between these two phases and to the relationships between microregions within each phase; second, the macroequilibria and the microequilibria may be of a different specific character in spite of the fact that similar statistical mechanical considerations may be involved. Unfortunately, this suggestion cannot be adequately discussed nor can its meaning be clarified at this point. The consideration of this question will be resumed in the final paragraphs of this paper.

Donnan equilibria

The clay particles in the colloid phase of figure 1 cannot pass through the membrane because they are larger than the pores in the membrane. The small Na and Cl ions are not directly hindered by the membrane from passing through freely, and they will diffuse through the membrane until, in time, the net movement of these ions will cease and the system will have attained a steady state.

Whenever ions or molecules diffuse freely within a system until a steady state has been reached, we are accustomed to saying that the system has come to equilibrium. A Donnan system is therefore said to be at equilibrium with respect to the diffusible ions when it is in a steady state, and this equilibrium is called a *Donnan equilibrium*. It should be remarked that, since the colloidal

particles cannot diffuse freely, the system is never at equilibrium with respect to them and that the Donnan equilibrium is therefore a partial equilibrium, as has been noted by Guggenheim (11).

The Donnan equilibrium is a very special kind of equilibrium because the small ions are free to move only in the sense that the membrane offers no direct impediment. They are restrained from absolutely free movement by the charge on the particles and therefore may be prevented from attaining a purely random distribution like that reached by sucrose after diffusion through a column of water. The number of positive charges in each phase must be equal to the number of negative charges because each phase must be electrically neutral.

In 1911 Donnan (3) presented the results of a first attempt to investigate theoretically the distribution of ions between the various phases of Donnan systems at equilibrium. Since that time, Donnan and many other workers have investigated the relative concentrations of diffusible ions in the phases of Donnan
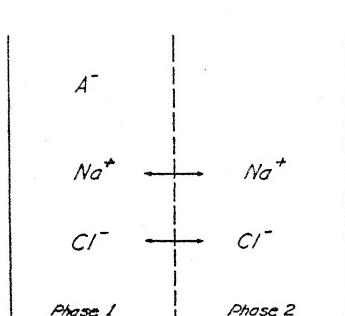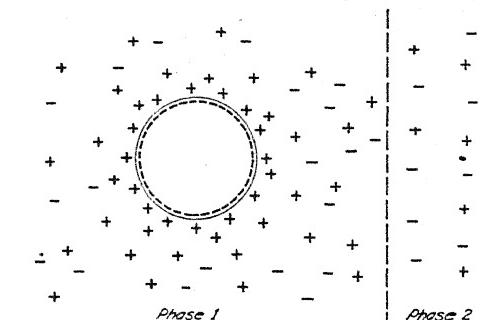
FIG. 1.   FIG. 2.

FIG. 1. DIAGRAMMATIC REPRESENTATION OF A DONNAN SYSTEM CONTAINING SODIUM CLAY AND NaCl

FIG. 2. DIAGRAMMATIC REPRESENTATION OF A CLAY PARTICLE IN A DONNAN SYSTEM AT EQUILIBRIUM

systems and the so-called membrane potentials, both theoretically and experimentally. A definite formulation of these relative concentrations in the case of real systems is attended with much more difficulty than is apparently realized by many workers in the biological sciences and in soil science. The nature of these difficulties, and some of the reasons for them, will be discussed later.

Donnan (3) and later Donnan and Guggenheim (6) and others investigated the thermodynamic principles involved in Donnan equilibria independently of ionic concentrations or membrane potentials. A thermodynamic treatment has been very exactly set forth by Donnan and Guggenheim, and it is proper to say that this problem has been solved.

It is customary in discussions of Donnan equilibria, first to present a hypothetical description of the expected distribution of ions between two phases in a Donnan system. Whenever one critically considers these discussions, it becomes apparent that the phases are tacitly assumed to be perfect or ideal solutions, although this fact is not always brought to the attention of the reader.

Subsequently, a more general thermodynamic discussion commonly is presented, usually rather briefly. The entire treatment has the disadvantage that it tends to leave the impression that the description in terms of ideal solutions is generally adequate and that the thermodynamic discussion is somewhat of a concession to those who insist on rigorous analysis.

Unfortunately, at least in the case of clay suspensions, colloidal systems are apparently very far from being composed of ideal solutions; the usual elementary discussion, therefore, is not merely slightly incorrect but may be totally inadequate. An adequate treatment may be based either upon thermodynamics or upon a detailed investigation of the factors involved in the concentrations of ions in real colloidal systems. The two methods are radically different in character and will be discussed separately. The thermodynamics of Donnan equilibria are developed in the following sections. The discussion is based upon the treatment of this problem by Donnan and Guggenheim (6). The terminology, however, is that of Lewis and Randall (17), which is more familiar to Americans than that employed by Donnan and Guggenheim.

Thermodynamic discussion of Donnan equilibria

The primary condition for equilibria of all types is that for any infinitesimal process occurring in a system at constant temperature and pressure, the free energy change, dF, must be zero. In the case illustrated in figure 1, let us consider an infinitesimal process consisting of the transfer of Na ions from left to right. If the system is at equilibrium, the free energy change will be zero. Likewise the free energy change per mol of Na ions transferred, or in other words, the change in partial molal free energy of Na ions, $d\bar{F}_{Na}$, will be zero. The partial molal free energy, $\bar{F}_{Na} = \partial F/\partial n_{Na}$ of the ionic species, Na, must therefore be the same in both phases.[3] Similar considerations hold for Cl ions and for the molecular species, NaCl, but not for the colloidal particles.

For NaCl we may write

$$(\bar{F}_{NaCl})_1 = (\bar{F}_{NaCl})_2 \qquad (1)$$

From the definition of activity given by Lewis and Randall (17)

$$\bar{F} - \bar{F}^\circ = RT\ln a, \qquad (2)$$

where a and $\bar{F}$ are the activity and partial molal free energy respectively, of a component in the system and $\bar{F}^\circ$ is the partial molal free energy of this component in a suitably chosen standard state, we obtain the equation

$$(a_{NaCl})_1 = (a_{NaCl})_2 \qquad (3)$$

This equation may be generalized and expressed verbally as follows: The activity of a diffusible electrolyte has the same value in all phases of a Donnan system at equilibrium.

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[3] This definition of ionic partial molal free energy is consistent with the definition of $\bar{F}$ for molecular species given by Lewis and Randall. It is identical with the electrochemical potential, $\bar{\mu}$, of Guggenheim, (10) but differs from the definition of ionic free energy implied by Taylor (26). The latter definition is apparently equivalent to the chemical potential, μ, as defined by Guggenheim.

In general, the partial molal free energy of the components of a system are functions of the concentrations of the components and of certain other factors which affect the energy of the system, such as temperature, pressure, hydration of solutes, potential energy due to interaction of molecules or ions, and potential energy in an imposed force field. These factors cannot all be evaluated, but their total effect can be estimated in favorable cases. It is customary to consider the total effect upon the activities, rather than upon the partial molal free energy of components. In the case of electrolytes, particularly strong electrolytes, Lewis and Randall (17) have presented the term "activity coefficient" to express the effect of such factors. The activity of an electrolyte may be defined, then, by the expression

$$a_{NaCl} = m_{Na} \cdot m_{Cl} \gamma^2_{NaCl} \tag{4}$$

where m is the molality of an ionic species and γ is the activity coefficient of the electrolyte. The mean activity is defined as

$$a_{\pm} = a_{NaCl}^{1/2} = (m_{Na} \cdot m_{Cl})^{1/2} \gamma_{NaCl} \tag{5}$$

Equation (5) then becomes

$$[(m_{Na} \cdot m_{Cl})^{1/2} \gamma_{NaCl}]_1 = [(m_{Na} \cdot m_{Cl})^{1/2} \gamma_{NaCl}]_2 \tag{6}$$

From similar equations involving other ionic species, it is possible to derive useful expressions, such as

$$\frac{(m_{Na} \gamma^2_{NaCl})_1}{(m_{Na} \gamma^2_{NaCl})_2} = \frac{(m_K \gamma^2_{KCl})_1}{(m_K \gamma^2_{KCl})_2} = \frac{(m_{Ca} \gamma^3_{CaCl_2})_1^{\frac{1}{2}}}{(m_{Ca} \gamma^3_{CaCl_2})_2^{\frac{1}{2}}} = \frac{(m_{Cl})_2}{(m_{Cl})_1} \tag{7}$$

Since these expressions involve the activity coefficient of the electrolytes and the concentrations of ionic species, the terms are measurable and these expressions may be utilized in the study of Donnan equilibria.

Donnan equilibria in ideal systems

Whenever the activity coefficient of NaCl is the same in both phases, equation (6) may be written

$$(m_{Na} \cdot m_{Cl})_1 = (m_{Na} \cdot m_{Cl})_2 \tag{8}$$

This expression is known as the ion concentration product principle. In discussion of this principle, it is not always clear whether summation concentrations of associated and dissociated ions or concentrations of dissociated ions alone are implied. As used here the terms refer to summation concentrations, although in the case of a strong electrolyte, which is completely dissociated, they also refer to dissociated ions.

A Donnan system for which equation (8) is valid may be defined as an ideal Donnan system. In principle it is not necessary that the individual phases be ideal systems. Systems of this type may conceivably be approximated by several cases: (a) Both phases consist of colloids of the same sign, the equivalent concentration of the colloid being nearly the same in both phases. (b) The concentrations of colloid are different, but a nondiffusible, nonelectrolytic solute is

present in one phase only. The presence of such a solute alters the activity coefficient of the electrolyte. The concentration of the solute is such as to bring the activity coefficient of the electrolyte in that phase to nearly that in the other phase. (c) The colloid in one phase is of the opposite sign from that of the other phase. The concentrations of ions may be very different in the two phases, but the activity coefficients of ion pairs may be nearly the same. (d) Interaction of ions and colloidal particles is at a minimum, or (e) all colloid phases are very dilute sols. In the last two cases the colloid phases are approximately ideal.

It should be emphasized that these cases are not purely hypothetical. It is probable that examples of both (a) and (b) may be found in the system plant root-soil colloid. Many of the data obtained by various workers, e.g., Greenberg and Greenberg (9), approximately verifying the ion product principle, equation (8), were probably obtained either from systems in which the interaction between ions and particles was at a minimum because of the small size and charge of the particles or from rather dilute systems. From equation (7) and similar expressions, we may derive the relations, valid only for ideal systems,

$$\frac{(m_{Na})_1}{(m_{Na})_2} = \frac{(m_K)_1}{(m_K)_2} = \frac{(m_{Cl})_2}{(m_{Cl})_1}, \quad \text{etc.} \tag{9}$$

Since the number of equivalents of positive and negative electricity must be equal in each phase, we may write

$$(m_{Na})_1 = (m_{Cl})_1 + (m_A^z)_1 \tag{10}$$

$$(m_{Na})_2 = (m_{Cl})_2 \tag{11}$$

when m^z represents the number of equivalents of exchangeable cations per 1000 gm. of water. Therefore, in any ideal colloid system in which the concentration of a colloid is large compared with that of the added electrolyte, we derive expressions such as

$$(m_{Na})_1 \gg (m_{Na})_2 \quad \text{and} \tag{12}$$

$$(m_{Cl})_1 \ll (m_{Cl})_2 \tag{13}$$

These inequalities are usually considered as characteristic of Donnan equilibria. Nevertheless they apply strictly only to ideal systems. The possibility of their application to real systems cannot be treated by thermodynamic methods, but will be discussed later.

Individual ionic activities

In this discussion we have considered the activities of electrolytes, i.e., of ion pairs, such as NaCl, but nothing has been said about the individual activities of the various ionic species. The terms so far discussed are all rigorously definable, and, at least in principle, the values of the quantities (or, more generally, differences between the values in two phases or two energy states) can be determined.

From the viewpoint of thermodynamics the valid, completely defined relations are of profound importance. From the viewpoint of the physical chemistry of

colloids, however, their usefulness is rather limited. We are usually interested in those properties of colloids, such as ionic adsorption and exchange and flocculation, which are affected by the individual ionic species. This tendency is clearly exhibited by Mattson, who deals almost exclusively with the concentrations and individual activities of ions.

Although individual ionic activities are discussed freely by many soil scientists and biologists and by some physical chemists, the prevailing viewpoint of those who have given special attention to the thermodynamic treatment of electrolytes, e.g., Guggenheim (10) and McInnes (18), is that the individual ionic activities are not definable quantities. Let us consider some of the difficulties involved in an attempt to define individual ionic activities, particularly with reference to Donnan equilibria, and why these difficulties are not encountered in defining the activities of complete electrolytes.

The fundamental definition of activities given by Lewis and Randall (17) is equation (2). The activity of an electrolyte may be defined in accordance with this equation or alternatively as a unique function of composition as in equations (4) and (5).

The mean activity, $a_\pm$, may be considered as a corrected or effective concentration. Many of the limiting laws of physical chemistry that are approximately valid only for very dilute solutions when expressed in terms of concentration may be cast into forms that are exact for all concentrations when activities are substituted for concentrations.

For complete electrolytes, e.g., NaCl, these definitions are consistent, and no difficulties are encountered in using them interchangeably. Let us consider two NaCl solutions at the same electrical potential. In one solution the molality of NaCl is m_1, the activity coefficient is γ_1, and the activity is a_1. In the other solution the respective values are m_2, γ_2, and a_2. If we transfer reversibly an infinitesimal amount of NaCl (or equivalent quantities of Na ions and Cl ions) from solution 1 to solution 2, the free energy change in the process is

$$\Delta F = (\bar{F}_2 - \bar{F}_1)_{\text{NaCl}} = RT\ln\frac{a_2}{a_1} = RT\ln\frac{(m_{\text{Na}} \cdot m_{\text{Cl}})_2\gamma_2^2}{(m_{\text{Na}} \cdot m_{\text{Cl}})_1\gamma_1^2} \qquad (14)$$

where the activities and activity coefficients are those of NaCl.

The activity coefficient of NaCl depends entirely upon the composition of the solution at any given temperature and pressure. Therefore the partial molal free energy and the activity of NaCl are unique functions of the composition of the solution.

Let us next consider the case of two NaCl solutions which, for any reason whatsoever, are at different electrical potentials. If we transfer NaCl, in the form of Na ions and Cl ions, from the solution of higher electrical potential to that of lower potential we must do work upon the system to cause the Cl ions to move against the potential difference. But an equal amount of work will be done by the system in the transfer of Na ions. The net electrical work is zero, and the free energy change is not affected by the electrical work done for each ionic species. Accordingly, in this case also, the difference in partial molal free

energies of NaCl and therefore the partial molal free energies and activities of NaCl in each solution are unique functions of composition.

When we attempt to transfer only Cl ions from one solution to the other, the work involved in the transfer and the free energy change in the process will depend upon the electrical potential difference between the two solutions. Even if the solutions were initially at the same potential, a potential difference will be set up as soon as only a very few ions are transferred.

The electrical work per Faraday equivalent of electricity transferred depends upon the opposing forces, e.g., upon the viscosity of the medium, and therefore is related to the mobility and transference numbers of the ions. But the electrical work per Faraday transferred is $\mathbf{EF}$, where $\mathbf{E}$ is the potential difference and $\mathbf{F}$ is the Faraday equivalent. Accordingly, the potential difference depends upon the transference numbers of the ions. In a 2-phase system with liquid-liquid junction, the transference numbers of the ions across the junction may vary with the character of the interface.

A Donnan system offers a rather pronounced illustration of this situation, since the mobility of the charged colloidal particles across the membrane is zero. In the case of a pure Na-clay suspension in one compartment and a different concentration of pure Na-clay suspension in the other compartment, the transference number of the clay particles across the membrane is zero and that of the Na ions is unity.

The preceding discussion may be summarized as follows: The partial molal free energy of an individual ionic species is a function of both the composition and the electrical potential of the solution. This functional relation may be expressed as follows in the case of Na ions,

$$\bar{F}_{Na} = l(\text{composition}) + L(\text{potential}) \tag{15}$$

The difference in electrical potential between two or more solutions and therefore the differences in individual ionic free energies depend upon the nature of the connections (e.g., liquid-liquid junctions) between the solutions.

Individual ionic free energies are thermodynamically definable in a purely formal sense. The definition of the partial molal free energy of Na ion in a solution containing such ions is for example

$$\bar{F}_{Na} = \frac{\partial F}{\partial n_{Na}} \tag{16}$$

where n_{Na} is the number of mols of Na ions added to a large amount of the solution. The potential between the two phases of a Donnan system at equilibrium (the so-called membrane potential) is considered thermodynamically undefinable. For this reason, membrane potentials have not been discussed. The functions (l and L) of equation (15) are generally regarded as not thermodynamically definable, and it probably may be safely concluded that their values cannot be measured by thermodynamic methods. Whether other methods are or will be available for the estimations of the values of these functions is disputable. Guggenheim (10) believes that such functions have no physical significance. McInnes (18), however, suggests that this may be an extreme view.

We may now proceed to the direct consideration of the definition of ionic activities. As we have seen, equations (2) and (16) express valid thermodynamic relations. It should therefore be possible thermodynamically to define ionic activities in accordance with equation (2), e.g.,

$$\bar{F}_{Na} - \bar{F}^{\circ}_{Na} = \frac{\partial F}{\partial n_{Na}} - \frac{\partial F^{\circ}}{\partial n_{Na}} = RT \ln a_{Na} \qquad (17)$$

Ionic activities so defined would depend upon the electrical potential of a solution and are not unique functions of composition. In a 2-phase system at equilibrium the activity of an ionic species would be the same in all phases. In particular, the activity of any diffusible ion in a Donnan system at equilibrium would be the same in all phases.

Apparently there have been few consistent attempts to define ionic activities in this manner. Although, in 1935, Rabinovitsch and Kargin (24) implicitly subscribed to this definition in relation to the "activities" of H ions at various distances from a particle in a colloidal suspension, in other papers, Rabinovitsch and his school have indicated that they consider the activities of ions to be different in the two phases of an equilibrium Donnan system (27).

As we have seen, the concept of activity possesses utility in two senses: first, as a measure of the driving force of a reaction or the escaping tendency of a component of a system, and second, as an effective or corrected concentration, i.e., as a unique property of a system independent of electrical or other potential gradients. Unlike the definitions of activities of molecules, the definition of activities of ions cannot cover both cases.

Almost exclusively the discussion of ionic activities in the literature has centered about the latter viewpoint (7, 10, 26). From equation (4) we realize that this concept is equivalent[4] to the identity

$$l(\text{composition}) = RT \ln a_{Na} \qquad (18)$$

This identity is not, however, a thermodynamic definition, since neither term can be defined independently.

It may be concluded, therefore, that the concept of individual ionic activities, as it has generally appeared in the literature, has no thermodynamic definition. This is regretable, since the term "activity" was introduced by Lewis (17) as a thermodynamic function. The significance of the concepts and alleged measurements of ionic activity will be considered later in the discussion of extra-thermodynamic aspects of Donnan equilibria.

Certain valid formal expressions involving ionic activities have been derived and frequently appear in the literature. These expressions involve identities between completely defined terms and products or ratios of undefined terms. By assigning arbitrary values to the undefined terms the equations can be satisfied.

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[4] Our terminology is correlated with the more precise terminology of Guggenheim (10). The definition (17) corresponds to $\bar{\mu}_{Na} - \bar{\mu}^{\circ}_{Na} = RT \ln a_{Na}$, which is not utilized by Guggenheim. Equation (18) corresponds to $\mu_{Na} - \mu^{\circ}_{Na} = RT \ln a_{Na}$.

Among the valid thermodynamic relations that may be satisfied in this way, the following may be considered: Formally, it is possible to define the *product* of individual activities of ions of opposite sign, as for example

$$a_{\text{NaCl}} = a_{\text{Na}} \cdot a_{\text{Cl}} \qquad (19)$$

The following *ratios* are defined:

$$\frac{(a_{\text{Na}})_1}{(a_{\text{Na}})_2} = \frac{(a_{\text{K}})_1}{(a_{\text{K}})_2} = \frac{(a_{\text{Ca}})_1}{(a_{\text{Ca}})_2} = \frac{(a_{\text{Cl}})_2}{(a_{\text{Cl}})_1} \qquad (20)$$

To summarize the thermodynamic properties of Donnan systems: the concentrations of electrolyte and of ionic species are thermodynamically defined quantities, since they can be experimentally determined. There are, however, no thermodynamically rigorous formulas relating the concentrations alone of ions in various phases of real Donnan systems at equilibrium. Rigorously derived formulas relating ionic concentrations and activity coefficients of electrolytic ion pairs are available. The activities of electrolytes are definable functions of partial molal free energies or of concentrations and activity coefficients of electrolytes. Thermodynamically valid formulas relating the activities of the electrolytes in various phases of real Donnan systems at equilibrium can be derived. The individual activities of ionic species cannot be defined as functions of concentrations of ions. Certain functions of activities of pairs of individual ionic species can be defined formally. Such formulas have no advantage over functions of activities of electrolytes.

APPLICATIONS OF THERMODYNAMIC RELATIONS TO DONNAN SYSTEMS

Approximately ideal Donnan systems

In elementary discussions of Donnan equilibria in textbooks of physical chemistry, e.g., Getman and Daniels (7), it is customary to derive and expound only certain relations between ionic concentrations similar to equations (8), (9), (12), and (13). This example is followed by many colloid chemists, e.g., Kruyt (15); biologists, e.g., Gortner (8); and pedologists, e.g., Mattson (in papers prior to 1938). Frequently the reader is not even provided with the intimation that these principles apply only to ideal systems. In other cases, one is led to infer that although it would be better to substitute activities for concentrations, this substitution constitutes a refinement of only minor importance.

Although Donnan recognized from the first that the exact thermodynamic conditions for Donnan equilibria should be stated in terms of activities rather than concentrations, he naturally desired to test his theory by approximate methods dealing with the easily measurable concentrations of ions. The earlier theoretical treatment of Donnan systems was concerned largely with the derivation of those relations, such as the ion concentration product principle, which are valid for ideal systems. All of the earlier, and much of the more recent work, has been carried out with the objective of verifying principles of this type in much the same spirit as that which motivated earlier physical chemists in the experi-

mental study of the gas laws, that is, those laws which apply strictly only to perfect gases.

Donnan and Allmand (4) in 1914 presented the results of measurements of the concentrations of K and Cl ions in the two compartments of a membrane cell. Potassium ferrocyanide was present in one compartment. The membrane was of copper ferrocyanide, through which the ferrocyanide ion cannot pass. In a series of ten measurements, the ratio of c_K/c_{Cl} in the $KCl + K_4Fe(CN)_6$ solution to that in the KCl solution was 1.10. The ion concentration product principle appears to have been approximately verified, although the agreement was not exact.

Similar results have been obtained by Donnan and Garner (5), who also studied a cell in which amyl alcohol was used as a membrane. Greenberg and Greenberg (9) obtained distribution ratios of Na and Cl ions in Na-caseinate systems which apparently indicated that such sols may be approximately ideal.

Real Donnan systems

The principles evolved in the thermodynamic discussion of Donnan equilibria can be applied to real Donnan systems. The significance of the statement that the partial molal free energy of an ionic species is the same in all phases at equilibrium may be easily realized by consideration of the electromotive force of a cell involving a Donnan system.

A galvanic cell may be arranged by placing an electrode, reversible to one of the ionic species of the system, in the colloid phase and an identical electrode in the noncolloid phase. If the two electrodes are connected to a potentiometer, an infinitesimal process may be said to occur when the potentiometer is so adjusted that no current flows through a galvanometer in series with the electrodes. The electromotive force of this cell may be evaluated in terms of the free energy change of the process as follows

$$\mathbf{E} = -\Delta F/N\mathbf{F}$$

where $\mathbf{E}$ is the electromotive force, N is the number of equivalents transferred and $\mathbf{F}$ is the Faraday equivalent. Since, at equilibrium, ΔF is zero, $\mathbf{E}$ must be zero also. (The e.m.f. or potential drop between the two identical electrodes should not be confused with the membrane potential.)

The following experiment illustrates this principle: Donnan systems were set up, utilizing pure Na-bentonite prepared by electrodialysis of natural Wyoming bentonite followed by the addition of carbonate-free NaOH to a pH of 7.2. At this pH value the replaceable Na content of the bentonite was 72.75 m.e. per 100 gm. Three suspensions containing different amounts of NaCl were prepared. Each suspension contained 6.87 mgm. of bentonite (oven-dry basis) per cubic centimeter of suspension. The concentrations of ions were corrected for the volume occupied by the particles with reference to the following considerations: Hofmann and Bilke (13) have determined the specific gravity of hydrated H-bentonite to be 2.1. This value is probably fairly close to that for Na-bentonite and was used in the calculation. These authors also estimated,

upon the basis of this density and from x-ray studies of the expansion of the montmorillonitic lattice of Na-bentonite upon hydration, that Na-bentonite probably holds within the lattice about 0.35 gm. of water per gram of hydrated clay. The volume of the hydrated clay in the suspensions was calculated to be 0.00443 cc. per cubic centimeter of suspension. The corrected concentration of compensating Na was calculated to be 5.025 m.e. per liter of the aqueous phase. The concentration of NaCl and the total Na concentration were likewise corrected.

Each suspension was placed in turn in one compartment of a membrane cell and separated from an NaCl solution by a collodion membrane. After some preliminary experimentation, three systems were brought to equilibrium. A silver–silver chloride electrode was placed in each compartment of the membrane cell. The electrodes were connected to a potentiometer and the e.m.f. was determined. The total Na concentration and the Cl concentration in each compartment are presented along with the e.m.f. of each cell in table 1.

TABLE 1

Distributions of ions, potential differences between two Ag–AgCl electrodes, and membrane potentials of Donnan equilibrium systems

CONCENTRATIONS			P.D. BETWEEN TWO Ag–AgCl ELECTRODES	MEMBRANE POTENTIALS
In suspension		In external phase		
^cNa	^cCl	^cNaCl		
m.e./l.	*m.e./l.*	*m.e./l.*	*mv.*	*mv.*
5.199	0.174	0.24	0.0	7.0
6.103	1.078	1.18	0.0	1.4
15.15	10.12	10.70	0.0	0.6

No salt bridges were used in this experiment. In another experiment with these systems each phase was connected to a calomel electrode by means of a saturated KCl salt bridge. The P.D. between the two calomel electrodes was measured as the e.m.f. of the cell. This system contains three liquid–liquid junctions. The two salt bridge junctions may be assumed to be small and opposite in sign, and therefore their algebraic sum may possibly be neglected.

In this manner the potential drop across the membrane can be measured approximately. The potential drop across the membrane, or the membrane potential, is equal and opposite in sign to the algebraic sum of the Ag-AgCl electrode potentials. The membrane potentials are also presented in table 1.

We have seen that the partial molal free energy, or alternatively the activity, of a diffusible electrolyte has the same value in all phases of a Donnan system at equilibrium. The thermodynamically valid expression (6) was derived. The experimental results presented in table 1 can be applied to this formula for the determination of the activity coefficient of NaCl in the colloid phase. The concentrations of the ionic species and the products of these concentrations are presented in table 2. In table 3 are given the activity coefficients of NaCl

in the two phases and the ratios of these two activity coefficients. The values of activity coefficients for the pure NaCl solutions are interpolated from data of Lewis and Randall (17). The experimental values in table 2 are in equivalents per liter, whereas the activity coefficients of Lewis and Randall were based on molalities. For such dilute solutions the errors so introduced are probably well within the errors of measurements. The activity coefficients in table 3 are concentration activity coefficients, f.

The data presented in table 2 suggest that the ion concentration product principle is inapplicable to a real clay system. The low values of the activity coefficients of NaCl in those suspensions that contain small amounts of NaCl indicate that such suspensions are far from ideal. The activity coefficient of

TABLE 2

Donnan equilibrium distribution of Na and Cl in Na-bentonite systems

Concentrations in milliequivalents per liter

IN SUSPENSION			IN EXTERNAL PHASE	
c_{Na}	c_{Cl}	$c_{Na} \cdot c_{Cl}$	$c_{Na} = c_{Cl}$	$c_{Na} \cdot c_{Cl}$
5.199	0.174	0.905	0.240	0.0576
6.103	1.078	6.579	1.18	1.392
15.15	10.12	153.3	10.70	114.5

TABLE 3

Activity coefficients of NaCl in a Donnan system at equilibrium

Concentrations in milliequivalents per liter

IN SUSPENSION		IN EXTERNAL PHASE		$\dfrac{f'}{f^r}$
$c_{Na} \cdot c_{Cl}$	f'_{NaCl}	$c_{Na} \cdot c_{Cl}$	f^r_{NaCl}	
0.905	.250	0.0576	.989	.252
6.579	.449	1.392	.976	.460
153.3	.793	114.5	.918	.864

NaCl in the more concentrated solution is greater. As the ratio of NaCl to colloid increases, the suspensions approach pure NaCl solutions in character. The properties are dominated by the NaCl present.

EXTRATHERMODYNAMIC METHODS OF APPROACH TO THE PROBLEM OF DONNAN EQUILIBRIA IN REAL SYSTEMS

Degree of dissociation of colloids and interaction between ions and particles

In 1929 Mattson (20) published results similar to those presented in table 2. His experiments were carried out with Donnan systems prepared from natural bentonite gels and solutions of NaCl, $NaNO_3$, Na_2SO_4, and $Na_4Fe(CN)_6$. Although his tabulations do not include the products of the concentrations of ionic species, these values can be obtained from the data presented.

Instead of merely concluding that the ion concentration product principle was inapplicable, Mattson scrutinized the problem more closely. He assumed that the bentonitic colloidal electrolyte was incompletely dissociated and that the ion concentration product principle might be considered valid with reference to the concentrations of dissociated ions.

On the basis of this assumption, Mattson calculated the concentration, z, of Na ions dissociated from the clay particles in each suspension and the degree of dissociation of the bentonite. Similar calculations have been made for the bentonite suspensions that have been described in this paper. The apparent concentrations, z, of dissociated Na ions and the apparent degrees of dissociation of Na-bentonite are presented in table 4.

There is, however, no direct experimental evidence for the assumptions that were made by Mattson. On the contrary, as Mattson at once recognized, it seems surprising at first sight that the degree of dissociation should increase with the concentration of added electrolyte. One might expect the common ion, Na, to repress the dissociation. Mattson explains this apparent discrepancy

TABLE 4

Apparent concentrations of dissociated Na ions and apparent degrees of dissociation of Na-bentonite

TOTAL Na IN SUSPENSION	APPARENT CONCENTRATION (z) OF DISSOCIATED Na	APPARENT DEGREE OF DISSOCIATION OF Na-BENTONITE*
m.e./l.	*m.e./l.*	*per cent*
5.199	0.157	3.12
6.103	0.214	4.26
15.15	1.213	24.08

* Based on replaceable Na content of 5.025 m.e./l.

by the suggestion that in pure bentonite suspensions the colloid is only very slightly dissociated. He then further assumes that in the more concentrated salt solutions the potential of the colloidal particle is decreased by the added electrolyte. According to his theory the potential is not decreased because of discharge of the particles due to increased association of Na ions and particles but because of increased ionic interaction. When the potential is decreased, the counter ions are held less firmly and therefore tend to be more dissociated.

In a later paper (21) Mattson developed this point of view in relation to the theory of the "salt effect" on weak electrolytes and discussed the application of the Debye-Hückel theory to an interpretation of the effect of increased ionic strength on the dissociation of weak electrolytes. If direct measurements of the degree of dissociation of Na-bentonite were available it would be interesting to apply them to this theory. Possibly they would confirm it, at least qualitatively. But such measurements are not available. Mattson's calculated values are based upon the assumption that the ion concentration principle holds between the concentrations of dissociated ions present.

Mattson (19) presented calculations based upon determinations of zeta-

potential, which indicated a degree of dissociation of Na-bentonites of about 0.17 per cent. It seems fair to suggest that the significance of the concept of the zeta-potential is not clearly understood at present, and that calculations based upon the assumption that the zeta-potential indicates the binding force of particles for ions are of uncertain validity. Langmuir (16) has shown that although zeta-potentials calculated from particle mobilities in an electric field approach a limit of about 100 mv., the contact potential between particles and water may be as high as 400 mv.

There are good reasons for supposing that the degree of dissociation of colloids is probably greater than was assumed by Mattson. From the estimate of the degree of dissociation given by Mattson it can be calculated that the free hydrogen-ion concentration of a 1 per cent suspension of freshly electrodialyzed bentonite with particles having radii of 45.5 mμ, assuming a specific gravity of 2.5, should be 1.40×10^{-6} mols/l. The pH should, in this case, be not lower than 5.85 and would probably be very appreciably higher, since ionic interaction producing a diffuse ion swarm rather than a random distribution of H ions might be expected to decrease the effective concentration of the ions. The author has obtained pH values of 3.3 for 1 per cent electrodialyzed bentonite sols of particle radius about 60 mμ. A considerably greater dissociation of hydrogen bentonite than 0.17 per cent would certainly be indicated by such results. It is very probable that a sodium bentonite would be at least as greatly dissociated.

In any event, the exact degree of dissociation has not been independently calculated with certainty by Mattson, particularly not in the presence of added electrolytes. Accordingly, we are justified in emphasizing again that his assumption that the ion concentration product principle is valid for the concentrations of dissociated ions cannot be supported by the evidence presented. Finally, it should be noted, for the sake of clarity, that the suggestions and interpretations by Mattson are not purely thermodynamic in character, although it is not to be assumed that one may object to them for this reason.

The results obtained by Mattson and those presented by the author could be equally well explained upon the assumption that Na-bentonites are completely dissociated, but that, because of interaction between ions and particles, the suspensions are far from ideal systems. In a more recent paper (22) Mattson has suggested that "saloids" may be completely dissociated, but because of ion interaction are "effectively" incompletely dissociated. One could, of course, calculate the effective degree of dissociation. This procedure is, however, so arbitrary and so inconsistent with ordinary thermodynamic technique that it does not appear desirable. The values obtained would have a fictitious significance only. For this reason the well-recognized concept of activity coefficients is to be preferred.

Activities of ions in colloidal systems

In recent papers, Mattson has restated his equations in terms of ionic activities. Equations of the type which he presents are formally valid, but since

they are incompletely defined, their advantage over equations representing activities of electrolytes, which are completely defined, is doubtful. We should, of course, be interested in activities of ions and their ratios if we could measure the former and were convinced that they had physical significance.

Ionic activities are, however, frequently given nonthermodynamic definitions. Ionic activities may be defined as functions of the electromotive force of cells involving liquid–liquid junctions. The most familiar example of this procedure is that involved in the electrometric determination of pH. An electrode reversible to H ions, a reference electrode, and a salt bridge are employed. The thermodynamic description of this cell is incomplete because of the undefined character of the liquid–liquid junctions. There are certain types of cells with liquid–liquid junctions, i.e., cells with transference for which the e.m.f. is thermodynamically defined (11, 17, 18). These involve junctions between pure solutions of the same salt in the same solvent. A salt bridge does not satisfy this criterion. It is used because it is believed that the liquid junction potentials are greatly minimized and vary only slightly with the solution to be bridged. It must be realized that pH can be defined empirically, but not thermodynamically, according to McInnes (18), in the following manner:

$$\text{pH} = \frac{0.4343\,\mathbf{F}(\mathbf{E} - \mathbf{E}°)}{RT}$$

where $\mathbf{E}$ is the electromotive force of the cell to be measured, R is the gas constand, $\mathbf{F}$ is the Faraday equivalent, and T is the absolute temperature. The term $\mathbf{E}°$ is an arbitrary constant. It may be considered as equal to the e.m.f. in a standard cell containing a solution, the pH of which is arbitrarily defined as zero, but it should not be confused with the standard electrode potential of the hydrogen electrode.

The term pH was first defined by Sorenson, as $\text{pH} = -\log c_H$. After the advent of Lewis' concept of activity it became fashionable to restate the definition as $\text{pH} = -\log a_H$. Since a_H is not defined independently, whereas pH is defined independently, although empirically, this procedure actually involves an attempt to define a_H empirically.

Empirically defined activities of other ions may be determined in a similar manner, but all activities so determined are dependent upon the values of the liquid junction potentials between the solution and the salt bridge.

In general such quantities cannot be uncritically applied to thermodynamic formulas. There are, however, applications that can be given a precise formulation. It is necessary, however, to eliminate (not merely minimize) liquid junction potentials including membrane potentials.

It has been pointed out by Taylor (26) and emphasized by Guggenheim (10) that no results of thermodynamic significance can be obtained by measurements of cells with liquid junctions that cannot better be obtained by measurements of cells without such junctions. Nevertheless, measurements of cells with liquid junctions have significance of a nonthermodynamic character. The prac-

tical importance of measurements of pH is generally accepted, for example; the theoretical significance however, is, not well understood.[5]

SIGNIFICANCE OF DONNAN EQUILIBRIA FOR REAL SYSTEMS

Qualitative and quantitative significance of Donnan equilibria

Generally speaking, pedologists have not directly applied the Donnan formulas to soil colloidal problems. Mattson, for example, has frequently presented such equations and explained their meaning. He has then proceeded to show that the expressions and their consequences are consistent in a qualitative manner with certain characteristics of soils which he has investigated.

In place of this procedure it would seem desirable to develop a thoroughly quantitative treatment, in which the experimental measurements can be applied directly to formulas expressing scientific laws. The desirability of this attitude seems particularly important when we consider the fact that we must frequently decide whether or not the data are actually explicable in terms of the Donnan equilibrium, or can best be explained by rival hypotheses. It has been ascertained by experiments of various authors that the filtrate from a sodium bentonite suspension, containing some NaCl, for example, will have a somewhat higher quantity of chloride per unit volume than the original suspension or the residue. Observations of this type have been explained by Mattson (20) as an instance of the Donnan equilibrium, by Alten (1) as due to a salt-free water skin, and by Hofmann and Giese (14) as due to hydration. Each of the authors presents carefully obtained numerical data; none of them was really able to show by the application of these data to precise formulas that his hypothesis is even tentatively adequate.

As we have seen, quantitative studies of the thermodynamic functions can be carried out, but they may be relatively unimportant. There is a further disadvantage in thermodynamic study of phenomena in complex systems. The fact has often been overlooked that expressions such as (1) and (6) are derived from a very general theorem, namely: The condition for equilibria *of all types* is that, for any infinitesimal process occurring in *any system*, the free energy change must be zero. This is the fundamental test for equilibrium and is applicable to all systems whether or not the equilibrium is purely of the Donnan type. It was pointed out by Hill (12) that the satisfaction of such criteria does not guarantee that the equilibrium state in a system is a Donnan equilibrium. Just as the qualitative approach may be unsatisfactory, thermodynamics may not always aid us in answering the more important and interesting questions. For example, let us again consider the theories of Mattson, of Alten, and of Hofmann and Giese. As far as thermodynamics is concerned, a colloidal

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[5] Scatchard has recently emphasized the importance of measurements which involve arbitrarily defined ionic activities. [Scatchard, G. *Science* 95: 27–32 (1942).] Marshall has measured the activities of ions in various systems. He uses clay membranes in somewhat the same way as the glass membrane of the glass electrode is used to measure pH values. [Marshall, C. E., and Bergman, W. E., *Jour. Phys. Chem.* 46: 52 (1942).]

phase might consist of (a) particles surrounded by thick polymolecular layers of pure water separating the double layer, the intermicellar region having the same composition as the liquid on the other side of the membrane; (b) hydrated particles surrounded by a rigid shell of hydrated ions; (c) incompletely dissociated "saloid" particles immersed in a liquid phase without discontinuities; or (d) completely dissociated particles, with electrostatic interaction between ions and particles. Nevertheless, the generalized conditions for equilibria apply to all such cases, and from thermodynamic considerations alone we could not choose between the various hypotheses. Baver and Winterkorn (2), on the other hand, have suggested that there are independent reasons for believing that such colloid phenomena as swelling are not entirely osmotic, i.e., cannot be explained in terms of Donnan equilibria.

Finally it should be pointed out that it may not be quite proper to speak of Donnan equilibria in natural soil systems. The application of the concept of Donnan equilibria to certain biological systems and to soil-plant relations considered as systemic units may well be justified because of the distinct separation between soil phase and plant protoplasm, between body cells and blood stream, etc. Soil systems found in nature are properly treated by soil physicists as 3-phase systems in the study of soil-moisture and soil-air relations. From the point of view required by the concept of Donnan equilibria, however, soil systems *per se* are 1-phase systems, since there is present no discrete noncolloidal macrophase upon which experiments can be performed. With the exception of special conditions, Donnan systems in the best sense do not exist in natural soil bodies or in the samples brought into the laboratory.

It is concluded that the significance of the Donnan equilibrium has been greatly overemphasized by the school of Mattson. The highly important investigations and numerous interpretative studies of that author and his followers have possibly lost as much as they have gained in significance and in rigorous treatment by the consistent attempt to relate them to the Donnan equilibrium.

Utilization of Donnan systems as experimental tools in the study of properties of soil suspensions

Although it has been suggested that the concept of Donnan equilibria should be confined to polyphase systems, it is undoubtedly true that the distribution of ions in the diffuse ion swarms of colloidal particles is statistically an equilibrium distribution. The analysis of such equilibria is of great importance for an understanding of the properties of soil suspensions, including soil in the natural state. In order to analyze the relation between such equilibria and Donnan equilibria, let us consider a schematic representation of a 2-phase Donnan system, figure 2.

A negatively charged particle is represented as present in the colloid phase. The particle is closely surrounded by positively charged ions. The density of positive ions decreases with distance from a particle, whereas the density of negative ions increases with distance. The electrostatic potential in the ion

swarm also varies with distance from the particle. The concentrations of cations and anions and the electrostatic potential in every small volume element, dv, in the system must have such values that the energy content of every volume element must be the same statistically when the entire system is at equilibrium.

Although this principle is anologous to thermodynamic criteria for equilibrium, the microequilibria cannot be directly measured and cannot be described by thermodynamic methods. It is necessary to utilize the methods of statistical mechanics, which are generally somewhat less rigorous than those of thermodynamics. The microenergy distributions can be integrated over an entire ion swarm or over the entire system. In the latter case, we may expect the results of the analysis to be identical with those obtained by thermodynamic methods.

The Debye-Hückel theory of strong electrolytes is a statistical mechanical theory of the ion swarms surrounding small ions in a solution. Some of the properties of such solutions can be derived, at least approximately, from other properties of such solutions as a result of an analysis by the method of Debye-Hückel. Müller (23) and others have applied this method to the ion swarm surrounding colloidal particles and to a derivation of relationships between the properties of colloidal suspensions.

The relations between the hypothetical microconcentrations in the volume elements dv and the measured concentration of ions in the suspension are rather complex. Although the measured value is an integral of the microvalues, the latter cannot be determined independently. On the other hand, the microconcentrations in the colloid phase are related to the microconcentrations in the noncolloid phase of an equilibrium Donnan system. But the latter values are essentially identical with the measured ionic concentration in the noncolloid phase.

It has seemed probable to the author that a theory relating the concentration of ions in the noncolloid phase of a 2-phase Donnan system to hypothetical microconcentrations and potentials as functions of distance from the particles could be developed and that the relationships involved in this case might be less complex than those considered by Müller and others. Integration of the microvalues over the entire colloid phase should give us the concentrations and electrostatic potential (membrane potential) of the colloid phase, which are measurable quantities.

It is desirable to point out that in the procedure suggested above, a Donnan system is utilized solely as a methodological device for investigating the properties of colloidal suspensions. The colloidal suspension may attain a separate existence from the noncolloid phase when it is mechanically removed from the membrane cell. Subsequently identical suspensions can be directly prepared ad lib. This apparently trivial observation suggests the desirability of avoiding the implication that colloidal suspensions are necessarily Donnan systems per se or that their properties are controlled by or need be described as consequences of the Donnan equilibrium.

Langmuir (16) has conceptually utilized a 2-phase colloidal system with a semipermeable membrane as a means of theoretically relating the properties

of a dilute colloid phase to those of a more concentrated colloidal suspension, because direct analysis of the properties of the latter is relatively complicated. It may be suggested that such procedures offer more promise than the rather elementary qualitative application of the Donnan theory or the definite but somewhat sterile consideration of precise thermodynamic relations. In any event, a frankly nonthermodynamic approach is to be preferred to one which confuses thermodynamic methods with other techniques and which utilizes thermodynamic terms in a vague sense.

The author is preparing a paper which will represent an attempt to approach the interpretation of activity coefficients of electrolytes in colloidal suspensions, the pH of hydrogen clay suspensions, the potential at the surface of a particle, and the potential of the suspension, along the lines suggested above.

SUMMARY

A theoretical discussion of Donnan equilibria, based upon the exact thermodynamic treatment of this subject by Donnan and Guggenheim is presented. The more familiar terminology of Lewis and Randall is substituted for that of Donnan and Guggenheim.

The expression, *Donnan equilibria*, is applied only to equilibria between phases upon which measurements can be made and not to equilibria between microregions in a suspension such as the "micellar" and "intermicellar" regions.

It is shown that, for real systems, such approximate generalizations as the ion concentration product principle are not adequate. On the other hand, nothing is gained by substituting the term "activity" for "concentration" in a discussion, unless the quantities which have been measured are actually activities rather than concentrations.

Emphasis is placed upon the conclusions of Guggenheim that, whereas activities of electrolytes are thermodynamically definable, the individual activities of ions are not. It is suggested that the use of the concept of ionic activities be avoided.

It is pointed out that the valid thermodynamic relations have been infrequently studied experimentally and that although they are important as criteria for the existence of equilibria, their consideration does not yield much interesting information.

The use of the Donnan principle by pedologists has been essentially qualitative. In the absence of quantitative formulations it is to be doubted that soil properties can be adequately explained in terms of Donnan equilibria in preference to other hypotheses.

It is suggested that the importance of the Donnan equilibrium as a regulative principle in soil chemistry has been greatly overemphasized.

It is indicated that the Donnan equilibrium can be used as an experimental device in the study of certain soil colloidal properties.

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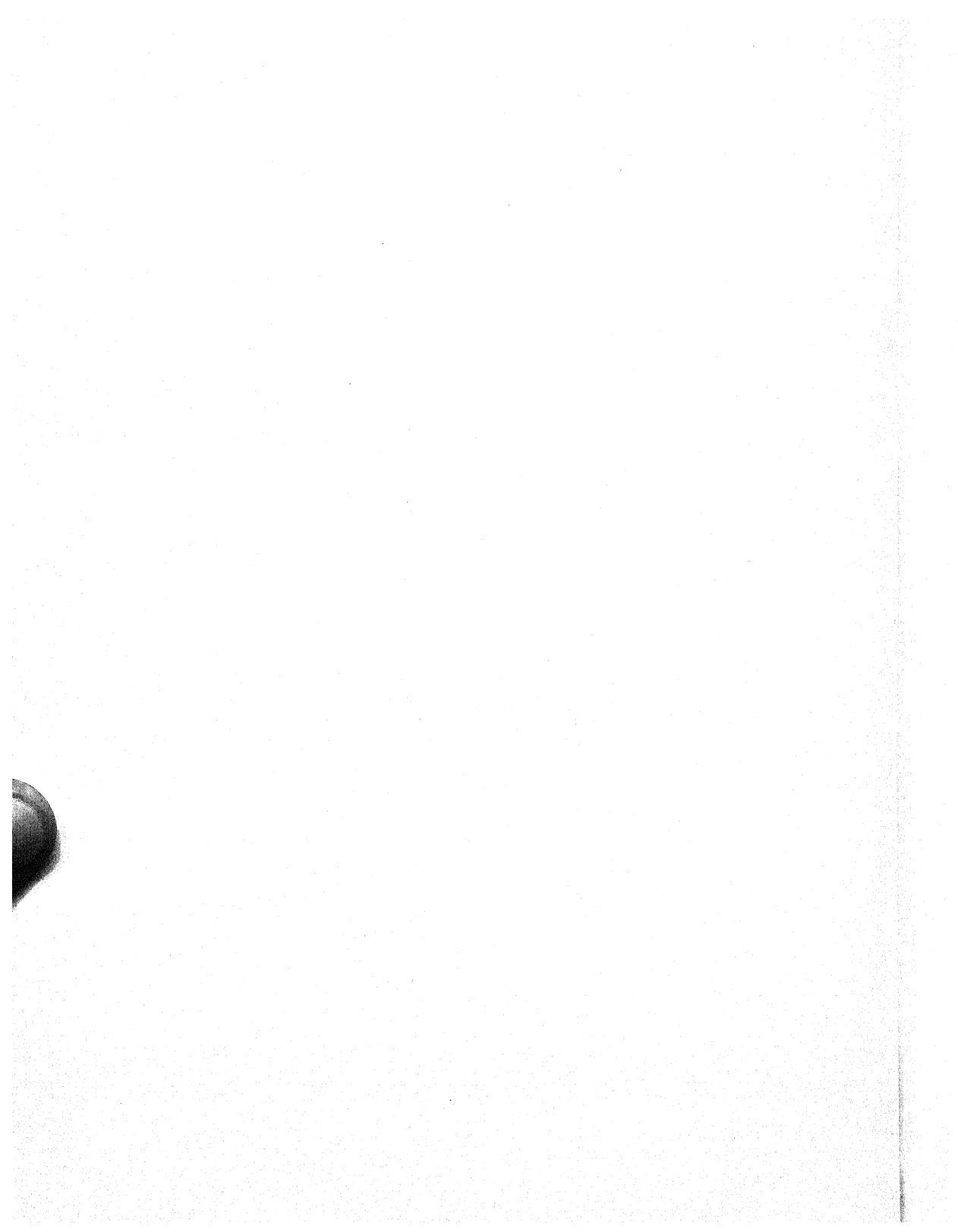
VOLUME–FREEZING-POINT RELATIONS OBSERVED WITH NEW DILATOMETER TECHNIQUE

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Much work has been done bearing on the dependence of the freezing point of soil moisture on moisture content (1–7, 9–17, 21–24). The experimental methods employed fall into two general classes: one is the Beckmann; the other, the dilatometer method.

It has been said (21) that permanent and irreversible changes are produced in the soil particles of a saturated soil by repeated freezing and thawing because experimental results obtained from consecutive runs on the same saturated soil sample are found to change progressively. Also, it has been said (4) that if the soil begins to freeze before equilibrium is attained with the bath used to supercool the moist soil, the results of successive runs will not check and will not be reliable. Preliminary investigations indicated to us that the observed irreversible changes are probably not in the soil colloids themselves. Instead, the changes are produced in part by the presence of tremendous amounts of dissolved air in the soil moisture which, upon freezing, expels the dissolved air to form, throughout the soil moisture, innumerable minute entrapped air bubbles the volume of which depends, according to Charles' law, upon the temperature of entrapment. If the dissolved air is not removed and if therefore the moist soil is not supercooled to the same temperature before each freezing, the results will be unreproducible because of the unreproducible total volume of the entrapped air bubbles. Even if the moist soil is always supercooled to the same temperature, the results will be unreliable if entrapped air bubbles are present. Also, the seemingly irreversible changes are produced, in part, by the formation of minute water vapor cavities around each soil particle whenever the temperature of the frozen moist soil mass is raised. The purpose of this article is to present the experimental results and the explanation of the multiplicity of volume–freezing-point relations to be observed by the usual dilatometer technique.

When water freezes, each gram expands 0.091 cc. If the total amount of water added to a dry soil placed in a dilatometer is known as well as the expansion of the soil-water mass when the freezable moisture freezes at a given temperature, one can calculate both the amount of freezable and the amount of unfreezable moisture at the given temperature.

The standard laboratory practice of drying soil does not completely dry the soil, and therefore the unfreezable moisture, calculated above at the given temperature, does not include all the unfreezable moisture present in the soil. The customary datum of zero-soil-moisture content is usually regarded as the state of the soil reached after prolonged drying at 110°C. This is not the absolute zero of soil-moisture content. The soil, dried at this temperature, still

contains a great deal not only of what is called crystal-lattice water but also of adsorbed water (18, 19, 20). Consideration of the dehydration curves of different soils shows no valid reason (except for the decomposition of organic matter) for choosing a temperature in the vicinity of 110°C. in preference to any other. The temperature of 110°C. was originally chosen probably because all soil moisture held below this point was thought to be free, and all above, bound. The uniformity in slope of the dehydration curves has now shown this idea to be erroneous. There is no point of inflection or marked change of slope of the dehydration curve indicating that the vicinity of 110°C. is of any special significance. The customary zero point of soil-moisture content is therefore an arbitrary datum whose only apparent justification at present is its analytical convenience.

Water freezes at any temperature above or below 0°C., depending on the condition to which it is subjected. Consider a mass of moist soil throughout which the moisture is at equilibrium. Although all parts of the soil moisture may be in thermodynamic equilibrium so that the escaping tendency and the total specific free energy of the water is the same throughout the soil moisture, the conditions that determine the freezing point of water vary widely throughout the water mass. Regions of the soil under the greatest adsorptive force, produced by the soil particles, and containing the greatest amount of dissolved material will have the lowest freezing point. In fact one finds that when the temperature of a mass of moist soil is lowered, the amount of moisture that will freeze at a given temperature, increases with decrease of temperature.

DILATOMETER TECHNIQUE

To eliminate the air in the soil moisture, we developed the following dilatometer procedure. Figure 1 represents the apparatus schematically. A known amount of distilled water is added from A to the highly degassed soil S in B, whereupon air-free kerosene from K is added to B until the meniscus in C is at the proper height. The temperature of the soil moisture in the dilatometer is varied by adjusting the temperature of the ice–salt-water mixture in V.

In more detail: a known weight of soil S is placed in the glass bulb B, which is sealed to the apparatus at L, whereupon the dilatometer B is evacuated by the pump P_1 after the stopcocks C_2, C_4, and C_6 are closed and C_3 and C_5 are opened. After most of the water and air are removed and while the pump P_1 is still running, B is surrounded by boiling water, and the evacuation is allowed to continue for 4 or more hours.

During this process, the still D and the burette A are evacuated by the pump P_2, stopcock C_2 having been closed and C_1 opened. In a short time, C_1 is closed and the electric heater H started, causing water vapor to distill over and condense in the previously calibrated burette A.

After the distilled water in A has cooled to room temperature and after the soil S has been subjected to 100°C. and about 1 mm. of pressure for 4 or more hours, stopcock C_3 is closed and C_2 opened, allowing a known amount of distilled water from the burette A to drain into B. C_2 is then closed.

To condense all the water drained from A on the soil S, an ice-salt bath must

be placed around S until all stray droplets on the sides of B or its stem have condensed on the soil.

While S is in the ice-salt bath, kerosene from K is added to B through C_3, completely filling the space below C_2, C_3, and the lower part of the capillary column C. Before the kerosene is added to B, any dissolved air is removed by pumping with P_1 while the kerosene is in K.
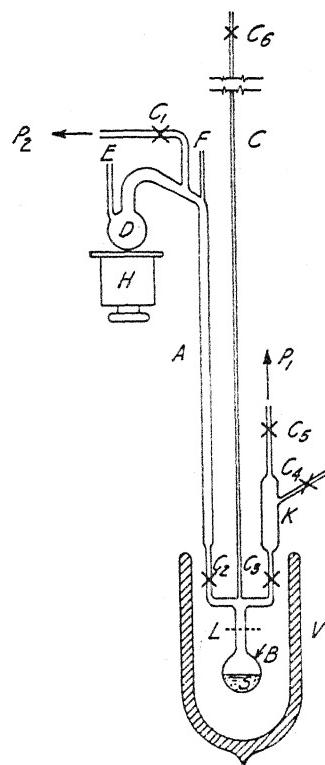
FIG. 1. DILATOMETER

A, burette to measure amount of water added to soil; B, bulb holding the soil under investigation; C, capillary tube (170 cm. long); D, still from which water is transferred to burette; E, opening to supply water to still; F, opening to allow cleaning of burette; H, electric heater for still; K, chamber holding kerosene; L, seal where bulb B is attached to apparatus; P_1 and P_2, to high-vacuum pump and aspirator respectively; V, Dewar flask holding constant temperature bath; $C_1 \ldots C_6$, stopcocks.

Care is exercised in adjusting the amount of kerosene below C_2 and C_3, in the bulb, and in the lower part of the capillary tube C so that when the entire system below C_2 and C_3 is immersed in the Dewar flask V containing an ice slush at 0°C., the meniscus of the kerosene in the capillary tube will be at a convenient height at all subsequent times of the experiment. Without this precaution it will be found that the meniscus will pass out the top or bottom of C for part of the temperature range in which the soil moisture is being studied.

All is now ready for the run. We ascertain the expansion of the moisture at different freezing temperatures by observing the change in position of the kerosene meniscus in the previously calibrated capillary tube C.

DILATOMETER MEASUREMENTS ON SOILS

A summary of studies of Aiken clay loam typical of a number of soils (the results of which are in as close agreement as those presented here) appears in figure 2. All of the curves in the figure were obtained from a great number of runs on the same sample of saturated soil. Before the beginning of each run, the entire sample was completely thawed.

Line S represents the volume–temperature relation of the soil–water system during supercooling. Positive and negative changes of volume of the dilatometer contents are measured with respect to the volume of the dilatometer contents at 0°C. Line I, parallel to S, represents the volume–temperature relation if all the water in the soil were free to freeze (that is, if no adsorptive forces and dissolved material were present to render some of the soil moisture unfreezable). It is determined by adding to the ordinate of each point of S, the quantity obtained by multiplying by 0.091 the total number of grams of water added to the dry soil. And finally, the family of curves below I represent measurements made in various ways on the soil sample.

If, for example, the temperature of the dilatometer is lowered to any temperature A and if crystallization is initiated, the volume will jump from the point A on the supercooling curve to a point B depending upon the temperature of the dilatometer after equilibrium is again established, that is, when the contents of the dilatometer come to the same temperature as the bath, which may not be at the same temperature as A. If now the temperature is raised, the volume relations are represented by the curve extending from B along C. As the temperature rises, the volume change approaches a maximum in the neighborhood of −1°C. and then decreases sharply along the curve H in the neighborhood of 0°C. The curve intercepts the temperature axis at $−\Delta T$°C., determined solely by the amount of dissolved material in the soil solution.

If supercooling and subsequent freezing are completed below about −9°C., the volume change with rise of temperature is represented by a point on D, the uppermost curve of the family. If now the temperature is gradually raised, the volume changes are represented by the uppermost curve, which at a point E, around −1.25°C., begins to turn down as did C.

No matter what equilibrium temperature (below approximately −9°C.) the soil experiences, a subsequent rise in temperature always causes the volume changes to follow the upper curve D. This behavior differs from that obtained when the lowest equilibrium temperature is above −9°C. In the latter case, a curve (such as C or G) followed upon rise of temperature depends entirely on the minimum equilibrium temperature (corresponding to B or F, respectively) experienced by the frozen soil. In other words, for experimental runs the minimum equilibrium temperatures of which are above about −9°C., we have a multiplicity of curves, the location of each depending upon the minimum equilibrium temperature experienced. Whereas for those runs the minimum

equilibrium temperatures of which are below about −9°C., we have but one curve.
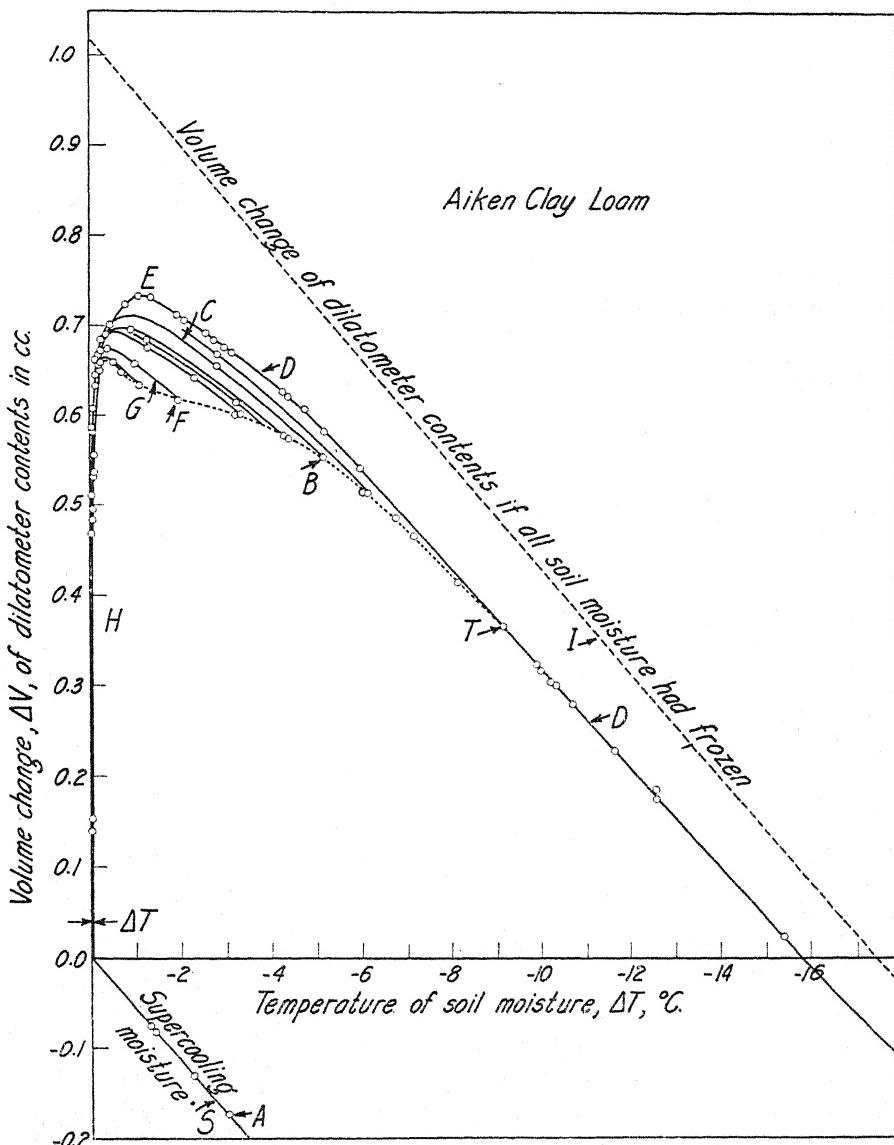
FIG. 2. DEPENDENCE OF CHANGES IN VOLUME OF DILATOMETER CONTENTS ON CHANGES OF TEMPERATURE FOR AIKEN CLAY LOAM (MOISTURE EQUIVALENT 28.98 PER CENT; PERMANENT WILTING PERCENTAGE 20.75 PER CENT), UNDER DIFFERENT FREEZING TREATMENTS *S*, the volume of supercooling; *I*, the volume change if all the water added to the dry soil were free to freeze

Consider the dotted curve, passing through points *F* and *B* and all other initial points of the family of curves. It is the locus of the initial point of each

member of the whole family of curves, because if the sample is supercooled to any temperature corresponding to B, for example, and if crystallization is initiated, the volume will always change to that of the point B on the locus. If then the temperature is gradually raised, the subsequent volume changes are represented by an extension of the solid line C having its initial point B on the locus.

The dotted curve is more, however, than the locus of the initial points of the family of curves. If we start a run by initiating freezing at a low temperature, then suddenly raise the temperature close to 0°C. and allow the freezing to be completed here, we can obtain the entire dotted curve in but a single run. By merely a lowering of the temperature (from the initial freezing temperature around 0°C.), the volume of the dilatometer contents so changes as to trace out the locus of the initial points of the family of curves.

The results for three other quite different soils show a similar family of curves for the respective soils. Each has a curve which is the locus of the initial points of the family and in each the family of curves are all parallel to the uppermost member.

Thus the dotted line below D is not only the locus of the initial points (minimum temperature of each member) of the whole family of curves, but it is also the locus of points obtained during a single run when the first equilibrium temperature is established close to 0°C. and the others during the run are taken at lower and lower temperatures.

If once equilibrium is established and if this happens to be the minimum equilibrium temperature experienced during the run, then the only way to remain on the locus is to lower the temperature progressively. In consequence of any rise in temperature, we proceed up from the locus along a member of the family of curves having its initial point on the locus corresponding to the minimum equilibrium temperature experienced by the sample since it was last thawed. Once equilibrium has been established at some minimum temperature T_m, only that portion of the locus lying below T_m can be obtained. To get as much of the locus during any one run as possible, therefore, we should make the first equilibrium point occur at as high a temperature as possible, that is, close to 0°C.

Figure 3 further illustrates the behavior of the volume changes experienced by partly frozen soil moisture with changes of temperature. If after supercooling so as to initiate freezing at a point such as B on the locus, we now raise the temperature, the volume changes will be as represented by the arrow on curve C. If the temperature is raised high enough, ΔV decreases and would eventually reach zero. If, however, the temperature is not allowed to rise until ΔV becomes zero but is made to decrease at some point such as J, we will not retrace the curve C. The new path, however, bears a remarkable relation to the locus. The return path will fall somewhat lower than the initial path C, but it will always fall above the locus until it eventually turns on it at a point K, the temperature of which is somewhat greater than that corresponding to B, the lowest past equilibrium temperature during the run. Further lowering of

the temperature will cause the volume change to follow continuously the locus without deviation. If we raise the temperature we move up one of the family
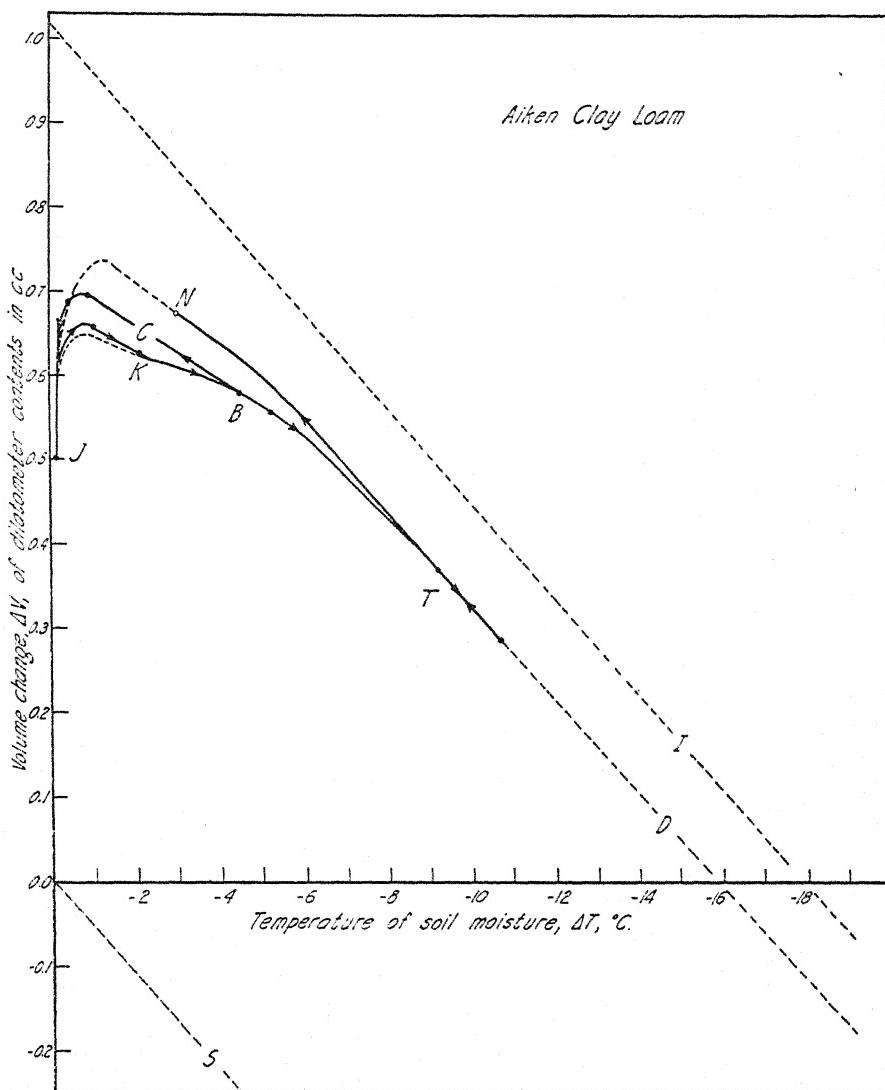
FIG. 3. SEEMINGLY IRREVERSIBLE VOLUME CHANGES OF AIKEN CLAY LOAM BROUGHT ABOUT IN THE DILATOMETER BY CHANGES OF TEMPERATURE

of parallel curves. If we lower the temperature (below about $-9°C.$) and then raise it, we move up the uppermost bounding member of the family of curves.

We thus discover, in studying the volume–freezing-point relations of saturated soil, that one curve called the locus of the initial points of the family of

curves has a most peculiar significance: it makes its appearance in many ways and enables us to construct and predict much of the location of the family of curves. It is such that a backward extension toward higher temperatures of the part of the envelope below about −9°C. gives the location, at least up to about −5°C., of the uppermost member of the family of curves. All of the other members are seemingly parallel to this uppermost member.

It has been said (4, 21) that permanent irreversible changes are apparently produced in soils by repeated freezings and thawings, and thus subsequent runs on the same sample did not agree with the initial, particularly for the finer-textured soils. The question might be raised whether the multiplicity of volume–freezing-point curves, just presented for the same soil sample, does not illustrate this irreversibility. Judging from our results, such is not the case: the curves obtained after 30 runs (made on the identical sample from which the results in figure 2 were obtained) extending over a period of more than $2\frac{1}{2}$ months coincide with the curves made under the same conditions at the beginning of the series of runs. The results for three other soils corroborate this.

A particular dilatometer measurement might fall anywhere between the envelope (fig. 2) and the uppermost curve of the family, depending on the freezing history subsequent to the last complete thawing of the soil moisture. The question arises, therefore, which among the multiplicity of curves should we take in describing the true volume–freezing-point relations of the saturated soil sample, and then what do the others mean? Previous workers (4, 5, 11, 12, 13) attach particular significance to the upper member of the family. This point of view would seem justified because once equilibrium has been attained at any temperature below about −9 or −10°C., we always trace out the upper member with rise of temperature. It has even been mentioned (4) that reproducible results are always obtained if the sample is first frozen below about −9°C. What interpretation should be placed upon the other members of the family as well as upon the envelope?

EXPLANATION OF REPRODUCIBLE FAMILY OF CURVES OBTAINED BY THE DILATOMETER

Figure 4 represents schematically a pair of soil particles in contact and surrounded by a film of water. Although the particles are represented as spheres, the following considerations are unaltered if the particles are irregular, as are soil particles.

Figure 4A represents the particles in the dilatometer where the soil is saturated and where, accordingly, the particles are completely immersed in water. The area with lines perpendicular to the soil-particle surface represents (not to scale) the water remaining unfrozen at a given temperature. It remains unfrozen because it contains dissolved material and because it is under pressure caused by the strong adsorptive field surrounding the soil particles. The area with the lines horizontal represents frozen water. The ice-liquid-boundary position is determined so that the total freezing-point depression ΔT of the solution, which is the sum of ΔT_P, due to hydrostatic pressure, and ΔT_o, due to osmotic pressure, is the same at all points of the ice-liquid boundary. Points

outside the surface are at too low a combined hydrostatic and osmotic pressure to remain liquid; points within, at too high a combined hydrostatic and osmotic pressure to remain solid at ΔT below 0°C.

As the temperature is lowered (fig. 4B), the ice-liquid boundary moves inward to a new surface of constant but greater freezing-point depression having a greater hydrostatic, as well as osmotic, pressure. Also, as the temperature rises (fig. 4C), the interface moves outward.

When the temperature is lowered (fig. 4B), what happens to the shell of ice that surrounds the unfrozen water adjacent to the soil particle? Since water expands upon freezing, should it not break the ice shell? Probably, but in so doing it forces liquid water out into the minute cracks and fills them. Water at the greatest distance from the soil surface should be the first to freeze, being under least osmotic and hydrostatic pressure. Thus as the ice-liquid interface advances radially inward, the salt in the liquid water of the cracks is returned and concentrated in the inner liquid layer surrounding the soil particle.
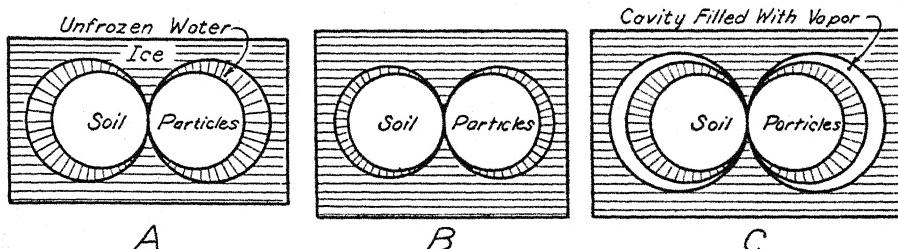
FIG. 4. SCHEMATIC DIAGRAM OF HOW VAPOR CAVITIES MIGHT BE FORMED AROUND SOIL PARTICLES BY FREEZING

(A) Part of soil moisture frozen; (B) Temperature lowered, causing the freezing of more soil moisture and a consequent increase in volume of the system; (C) Temperature raised to the initial temperature causing the melting of frozen moisture adjacent to unfrozen moisture and a consequent appearance of cavities of water vapor.

When the temperature is raised (fig. 4C), to the original value of figure 4A, a shell of ice surrounding the liquid layer adjacent to the soil particles will melt. Cavities will be formed between the vesicular rigid mass of solid ice and the unfrozen water shell surrounding the soil particles, because when ice melts the volume decreases 0.091 cc. per gram. The total apparent volume of frozen soil (fig. 4A) at a given temperature is therefore greater (fig. 4C) if it is first subjected to a lower temperature (fig. 4B). This is our basis of explaining the multiplicity of reproducible freezing curves obtained with the dilatometer.

Consider figure 2. The following considerations also apply to all other soils we have studied. Suppose we initiate freezing and arrive at equilibrium at point F around -2°C. If now the temperature is lowered, we slide down the locus. Suppose we stop at B and raise the temperature again to -2°C. We arrive at a volume C greater than at F, although the external pressure and temperature are no different. Had we not stopped at B, but continued to below -9 or -10°C., we should again, with rise of temperature, slide up the uppermost member of the family to a still greater volume at -2°C. Thus, the

lower the minimum equilibrium temperature (down to about $-9°C.$) experienced by the dilatometer contents during a run, the greater the size of the vapor-cavities surrounding each moist soil particle at the higher temperatures.

The cavities are not permanent at the higher temperatures, but can be made to collapse and disappear by thawing of the frozen soil. After each complete thawing of the vesicular ice mass, the saturated soil returns to its original state; and all its past, apparently irreversible history is obliterated. On the present sample of Aiken soil for instance, a series of 27 runs were made over a period of 70 days. The results obtained in the final run coincided with those obtained from the first runs (these runs being carried out under like conditions) when the frozen soil was completely thawed before each run. The results of as many of the 27 runs as could be plotted without confusion are shown in figure 2.

Judging from the parallelism as well as the prolonged straight-line nature of the whole family of curves, cavities are indeed forming as the temperature is raised. The volume changes observed are then mainly a measure of the temperature coefficient of expansion of pure ice and kerosene even as far up as $-1°C.$ Around $-1°C.$, however, with further temperature rise, the cavities have enlarged so greatly as to weaken the vesicular ice structure and cause it to collapse and the curves, therefore, to drop.

Also supporting the belief that cavities form with rise of temperature is the fact that the upper members reach their maximum height at lower temperatures than the lower members of the family of curves. Curve D, the uppermost member, for example, reaches its maximum near $-1.3°C.$, whereas the lower members reach their maxima at progressively higher temperatures, eventually crossing over the upper members. Thus very close to $0°C.$, the upper members of the family of curves indicate a smaller apparent amount of frozen moisture than the lower members. The explanation for this, we believe, is that at a given temperature the vapor cavities of the upper members are larger than those of the lower members of the family of curves. The ice walls of the vesicular honeycomb structure of ice surrounding the soil particles must therefore be thinner, more fragile, and more readily collapsible, permitting the cavities to be filled with liquid sooner and the dilatometer volume to collapse sooner to the true volume.

Previous workers have always used the uppermost curve of the family to describe the volume–freezing-point relations of a saturated soil sample. Our present considerations indicate that this leads to erroneous conclusions and that the envelope is the only curve enabling us to calculate, in the absence of cavities at a given temperature, the true percentage of unfrozen soil moisture in the dilatometer. All the others involve the presence of innumerable indeterminate water-vapor cavities surrounding the soil particles even though the dissolved air has been eliminated.

SUMMARY

Irreversible changes in the volume–freezing-point relations of a more than saturated soil are produced by the presence of tremendous amounts of dissolved

air in the soil moisture, which expels the dissolved air to form throughout the soil moisture innumerable entrapped air bubbles, the volume of which depends, according to Charles' law, on their temperature of entrapment. A new dilatometer technique enabling the elimination of the dissolved air is described.

Seemingly irreversible changes are produced by the formation of minute water-vapor cavities around each soil particle whenever the temperature of the frozen water-soil mass is raised. This gives rise to a family of parallel curves (representing the volume–freezing-point relations of the soil under all conditions) the initial points of which all lie on a locus, which alone, we believe, represents the true volume–freezing-point relations of the soil in the absence of cavities. This locus is, however, quite different from the one taken by others in the past as representing the true volume–freezing-point relations of a more than saturated soil. Two distinct ways are presented for obtaining this locus.

A theoretical explanation of the reproducible family of curves representing the true volume–freezing-point relations of a soil under all conditions is also presented.

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C.	Centigrade	m.e.	milliequivalent(s)
cc.	cubic centimeter(s)	mgm.	milligram(s)
cm.	centimeter(s)	ml.	milliliter
cu.m.	cubic meter(s)	mm.	millimeter(s)
F.	Fahrenheit	mμ	millicron(s)
gm.	gram(s)	N	normal (as applied to concentrations)
γ	microgram(s)		
kgm.	kilogram(s)		
m.	meter(s)	p.p.m.	part(s) per million
M	molar (as applied to concentrations)	sp.gr.	specific gravity
		sq.cm.	square centimeter(s)

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$$C_4 = \frac{R_1}{R_2} \cdot C_3 \qquad\qquad (2)$$

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THE EDITORS.

UTILIZATION OF ADSORBED PHOSPHATE BY COTTON AND OATS[1]

RUSSELL COLEMAN

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Despite the high phosphate-fixing capacity and the low content of readily available phosphate of certain Coastal Plain soils, many nonleguminous crops such as cotton, corn, and oats often fail to respond when soluble phosphate is applied, or fail to show phosphate deficiencies when phosphate is not applied. The failure of crops to respond to applied phosphate has often been attributed to its rapid fixation by the soil. The ability of plants to grow normally in soils with a limited amount of readily available phosphate suggests, however, that many plants can obtain sufficient phosphorus from the difficultly available sources already present in the soil.

Many studies have been made to determine the availability of phosphates that have been fixed by artificially prepared iron and aluminum colloids or artificially prepared minerals, but very few have been made to show the availability to plants of phosphates fixed by kaolinitic and montmorillonitic clays extracted from the soil. The purpose of this paper is to determine how well cotton and oats can feed upon adsorbed phosphate that is held by such kaolinitic and montmorillonitic clays.

LITERATURE REVIEW

Numerous investigations have already shown that soluble phosphorus is fixed in a difficultly available form as soon as it is applied to the soil. Since the iron and aluminum of the soil have been considered the principal agents for fixing phosphate, the availability of iron and aluminum phosphates to plants has been studied by many investigators. As early as 1907 Patterson (11) found that iron and aluminum phosphates were valuable sources of phosphorus. Ellett and Hill (4) studied the availability of different sources of phosphorus in the greenhouse and concluded that iron and aluminum do not fix phosphate into forms unavailable to plants. Truog (15) also found that for certain crops freshly precipitated iron and aluminum phosphates are good sources of phosphorus.

In 1922 Wiley and Gordon (17) studied the availability of adsorbed phosphorus by allowing plants to feed on phosphate that had been fixed by artificial iron and aluminum colloids. They found that plants could utilize phosphates that had been adsorbed by soil colloids and that could not be leached by water.

The earlier studies show that iron and aluminum phosphates are somewhat available to plants and suggest that iron and aluminum in the soil are not altogether responsible for the fixation of phosphate into unavailable forms.

Recently Murphy (9) showed that finely ground kaolinite fixes large amounts of phosphate and attributed the high phosphate-fixing capacity of southern soils to their kaolinitic minerals. In a comparison of the availability of phosphates adsorbed by kaolinite with that of phosphates adsorbed by montmorillonite, he found that plants could feed well on the latter but very poorly on the former. Murphy's studies indicate that the mineral complex itself fixes phosphate, of which the availability to plants is determined by the kind of mineral.

The readily available phosphorus of soils has often been determined by extracting it with dilute acid or alkaline solutions. Many different extracting solutions have been used. Fraps (5) has found that $0.2N$ HNO_3 is an excellent extractant for removing available phosphate from the soil. Truog (16) has used a $0.002N$ H_2SO_4 solution buffered to pH 3 to extract available phosphate; and many investigators have found a good correlation between crop yields and available phosphate as extracted by the Truog procedure. Burd and Murphy (1) have used a $0.1N$ NaOH solution to extract adsorbed phosphate from the soil. Morgan (8), Spurway (13), Thornton (14), Miles (7), and others (6) have also used various extractants and have found them helpful in determining the available phosphorus of certain soils.

<div align="center">EXPERIMENTAL</div>

<div align="center">*Materials and methods*</div>

Clay from the B horizon of Orangeburg sandy loam (the fine clay of which consists of practically pure kaolinitic minerals) and clay from the B horizon of Susquehanna clay loam (the fine clay of which consists of practically pure montmorillonitic minerals) were used in this study. In a previous study (2) the fine clay minerals of each soil were identified. In Orangeburg fine clay (B horizon) only kaolinitic minerals could be detected, and in Susquehanna fine clay (B horizon) only montmorillonitic minerals could be found.

The phosphate solution used for the fixation studies consisted of a H_3PO_4 solution, containing 326 mgm. per liter of phosphorus, which had been adjusted to pH 7 with NH_4OH.

After the phosphate had been adsorbed by the clay, four extractant solutions were used to remove the readily available phosphorus. A $0.002N$ H_2SO_4 solution was used exactly as described by Truog (16). A $0.2N$ HNO_3 solution was used as described by Fudge (6), the soil-acid ratio being 1:5 and the time of shaking 5 minutes. A $0.1N$ NaOH solution was used according to the Burd-Murphy procedure (1), the soil-alkaline ratio being 1:5 and the time of shaking 1 hour. In the fourth extraction method, the phosphated clay was washed first with water and then four times with 60 per cent alcohol.

Phosphorus was determined by both the A.O.A.C. ammonium molybdate method and by the Fiske and Subbarow method as modified by Parker and Fudge (10).

<div align="center">*Procedure*</div>

Clays were separated from Orangeburg sandy loam and from Susquehanna clay loam by saturating the soils with sodium, using N NaOH, dispersing in a

mechanical stirrer, shaking in an 18-liter carboy, and siphoning adequate amounts after the material ($< 2\,\mu$ in diameter) had settled according to Stoke's law. Each clay was evaporated to a suitable volume, and after the concentrations were determined, 10-gm. aliquots were placed in 100-cc. centrifuge tubes. The clay was saturated with hydrogen by washing with four 50-cc. portions of HCl (pH 2), and the excess HCl was removed by washing with methyl alcohol until all traces of chlorides were removed. Previous studies in this laboratory had shown that such a treatment did not reduce the phosphate-fixing capacity of the clay. The H-clays were then dispersed in 200 ml. of phosphate solution (containing 65.2 mgm. phosphorus), placed in a 500-ml. Erlenmeyer flask, and shaken for 48 hours on a rotary shaking machine. After the clays were saturated with phosphate, they were flocculated with about 1 gm. of NH_4Cl, placed in centrifuge tubes, and the phosphate not adsorbed was removed by washing first with water and then with four 50-ml. portions of 60 per cent alcohol. All of the phosphated clays were treated with a water-alcohol extraction to remove the phosphate in solution, and most of the clays were then subjected to the acid and alkaline extractions described above. The excess $0.2N$ HNO_3 and the $0.002N$ H_2SO_4 were removed by washing with five or more 50-ml. portions of alcohol. The clays extracted with $0.1N$ NaOH were flocculated with about 1 gm. of NaCl, and the excess salt and base were removed by washing five times with alcohol. All of the phosphate removed by both the water-alcohol and the acid or alkaline extractions was determined, and the phosphate held against these extractions was considered to be adsorbed.

After the clays were prepared and their pH values determined, they were mixed with 2,000 gm. of sand in 1-gallon pots. These pots, together with similar pots containing sand without clay, and sand plus untreated clays, were divided into two groups. In one, 12 oat seedlings were transplanted into each pot and allowed to grow for 3 months; in the other, four cotton plants were grown in each pot for 5 months. At the end of the growth periods the tops of the plants were harvested, dried, weighed, and analyzed for phosphate. All experiments with cotton and oats were conducted in triplicate in the greenhouse.

During the growth of the plants, the pots were supplied about twice a week with 100 ml. of a nutrient solution identical with Shive's Formula I (12), except that it contained KCl instead of KH_2PO_4. No phosphate was applied to any of the pots that contained clay with adsorbed phosphate. The pots that received a soluble phosphate were treated with 26.1 mgm. phosphorus by applying at eight different intervals during the growth of the plants 20 ml. of a $Ca(H_2PO_4)_2 \cdot H_2O$ solution containing 3.26 mgm. phosphorus. In pots supplied with phosphorus from other sources, the phosphorus material was mixed with all of the sand in each pot. The sand and sand-clay mixture in each pot were kept at an optimum moisture content throughout the experiments.

The pH of the acid-extracted clays was much lower and that of the alkaline-extracted clays was much higher than those extracted with H_2O, but after the neutral nutrient solution was applied to the pots several times, the sand-clay medium approached an equilibrium of about pH 6.8.

TABLE 1

*Utilization of different forms of phosphate by oats**

FORM OF PHOSPHATE	KIND OF CLAY	EXTRACTING SOLUTION	YIELD OF OATS†	IN-CREASE IN YIELD DUE TO PHOS-PHATE	PHOS-PHORUS IN SAND OR SAND-CLAY MIX-TURE	PHOS-PHORUS AB-SORBED BY PLANTS
			gm.	gm.	mgm.	mgm.
Adsorbed	Montmorillonite	0.002N H₂SO₄	3.33	2.37	11.4	3.4
Adsorbed	Kaolinite	0.002N H₂SO₄	3.91	2.85	14.9	3.4
Adsorbed	Montmorillonite	0.2N HNO₃	5.72	4.76	14.2	6.5
Adsorbed	Kaolinite	0.2N HNO₃	6.26	5.20	19.6	6.4
Adsorbed	Montmorillonite	0.1N NaOH	6.18	5.22	35.9	10.0
Adsorbed	Kaolinite	0.1N NaOH	4.84	3.78	21.4	5.7
Adsorbed	Montmorillonite	Water-alcohol	6.93	5.97	37.0	12.7
Adsorbed	Kaolinite	Water-alcohol	5.90	4.84	34.5	9.7
Soluble	Montmorillonite		5.21	4.25	26.1	8.0
Soluble	Kaolinite		5.78	4.72	26.1	8.3
No phosphate	Montmorillonite		0.96	....	....	0.7
No phosphate	Kaolinite		1.06	....	....	0.9
Monocalcium phosphate‡			7.53	6.54	32.6	14.0
Superphosphate‡			7.85	6.86	32.6	10.4
Ammonium phosphate‡			7.76	6.77	32.6	11.2
Ferric phosphate‡			3.70	2.71	32.6	3.7
Fluorapatite‡			1.50	0.51	32.6	0.9
Tricalcium phosphate‡			1.92	0.93	32.6	1.3
Nutrient solution but no P			0.99	....	....	0.8
No P, no nutrient solution			0.50	....	....	0.8

* Each result represents an average of three similar pot treatments.
† Dry weight per pot.
‡ These samples were prepared by W. H. Ross, Bureau of Plant Industry, U. S. Department of Agriculture, and were obtained from W. B. Andrews, soils department, Mississippi State College.

Results with oats

The results in table 1 show that oats grew well on adsorbed phosphate whether it was held by the montmorillonitic or the kaolinitic clay. The yields were not so high with adsorbed phosphate as with superphosphate, ammonium phosphate,

or monocalcium phosphate, but in most cases they were considerably higher than with iron phosphate, tricalcium phosphate, and flourapatite, and many times higher than with clays containing no adsorbed phosphate. The increased yield of oats due to phosphate, both with the montmorillonitic and kaolinitic clays, was dependent upon the amount and kind of adsorbed phosphate. In most cases, as the amount of adsorbed phosphate increased, the oat yields also increased.

Not only the amount of phosphate present, but also the manner in which it was adsorbed determined its use by the plants. For example, with the kaolinitic clay 19.6 mgm. phosphorus adsorbed against 0.2N HNO₃ increased the
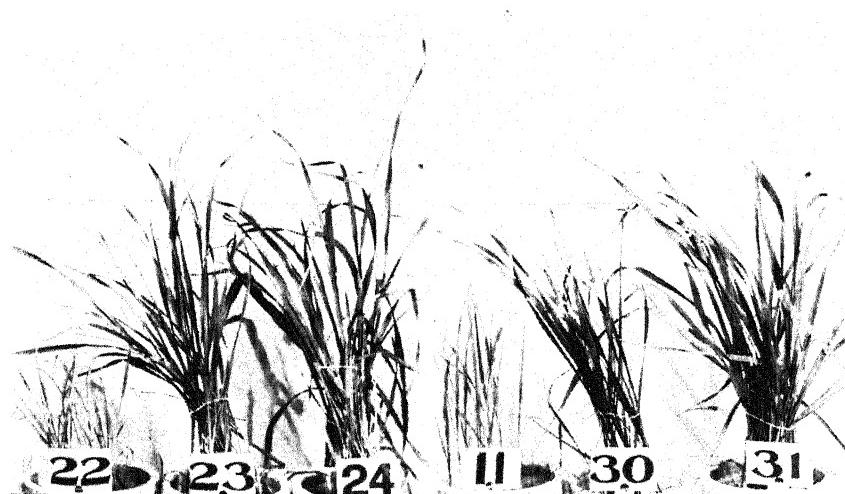
FIG. 1. EFFECT OF ADSORBED PHOSPHORUS UPON GROWTH OF OATS

Left, Sand + kaolinitic clay
Pot 22—No adsorbed phosphorus
Pot 23—14.9 mgm. phosphorus adsorbed
  against 0.002N H₂SO₄
Pot 24—19.6 mgm. phosphorus adsorbed
  against 0.2N HNO₃

Right, Sand + montmorillonitic clay
Pot 11—No adsorbed phosphorus
Pot 30—11.4 mgm. phosphorus adsorbed
  against 0.002N H₂SO₄
Pot 31—14.2 mgm. phosphorus adsorbed
  against 0.2N HNO₃

yield of oats by 5.20 gm., whereas 21.4 mgm. phosphorus adsorbed against 0.1N NaOH increased the yield by only 3.78 gm. This suggests that, with a kaolinitic clay, phosphate adsorbed against 0.1N NaOH was much less available than the same amount of phosphate adsorbed against an acid. The greatest increase in the yield of oats was obtained from the superphosphate mixed with sand. In this case 32.6 mgm. phosphorus yielded 6.86 gm. more than the pot containing no phosphate. The yields due to different phosphate treatments are difficult to compare since most of the pots contained different amounts and kinds of phosphate. The results show definitely, however, that the oat plant grew well on sources of adsorbed phosphate that are often considered unavailable to plants. Figure 1 shows the value of adsorbed phosphate to oats.

The fact that oats utilized the adsorbed phosphate is also shown by the large

amounts of phosphorus absorbed by the plants (table 1). These amounts were determined largely by the amount of adsorbed phosphate on the clay. Plants grown in pots with large amounts of phosphate absorbed more phosphate than plants grown in pots with small amounts of phosphate. In most cases as much as 30 to 40 per cent of the adsorbed phosphate was utilized by the plant.

Of the extracting solutions used, the $0.002N$ H_2SO_4 solution was most effective in removing the readily available phosphate from the clays, though even the method employing this extractant failed to remove all of the adsorbed phosphate which was available to oats. This suggests that even the stronger extracting solutions commonly used to remove readily available phosphorus from the soil do not remove all of the phosphorus which is available to certain plants.

Results with cotton

The dry weights of the cotton plants, as well as the increased yields due to phosphate, the phosphate adsorbed by the clay, and the phosphate absorbed by plants are shown in table 2. The yields show that cotton grew much better on all forms of adsorbed phosphate, whether it was held by the montmorillonitic or the kaolinitic clays, than it did on the clays containing no adsorbed phosphate. The increased yields due to phosphate were dependent upon the amount and kind of adsorbed phosphate present. In most cases, as the amount of adsorbed phosphate increased, the yield of cotton also increased.

In the case of the kaolinitic clays, the manner in which the phosphate is held also determines its use by the cotton plant. For example, cotton made as much growth on 16.9 mgm. phosphorus adsorbed against a $0.2N$ HNO_3 extractant as it did on 23.4 mgm. phosphorus adsorbed against a $0.1N$ NaOH extractant. These results with cotton, like those with oats, suggest that, with the kaolinitic clay, phosphate adsorbed against $0.1N$ NaOH extraction is much less available than the same amount adsorbed against an acid extraction.

Although the results in table 2 show an interesting relationship between the growth of cotton and its ability to utilize adsorbed phosphate, the data do not show the amount of fruit produced by the cotton plants. Since the number of cotton bolls produced by a plant determines its value, and since phosphorus plays an important part in the formation of the fruit, information on the fruiting of the cotton plants receiving different sources of phosphate should be of considerable value. Unfortunately, no record was kept of the number of cotton blooms or squares produced by each pot. In every case, however, where adsorbed phosphate was present the cotton produced fruit. Where no adsorbed phosphate was present the cotton produced no fruit. This observation is supported by figure 2. These results show that the cotton can grow and produce fruit on phosphate that is held rather strongly by the soil.

Of the methods used, Truog's removed the most readily available phosphate from the clay; however, the cotton plants seem to have grown very well on the phosphate adsorbed after the $0.002N$ H_2SO_4 extraction. More phosphate was adsorbed by the clays after the water-alcohol extraction and more cotton was

TABLE 2

*Utilization of different forms of phosphate by cotton**

FORM OF PHOSPHATE	KIND OF CLAY	EXTRACTING SOLUTION	YIELD OF COTTON†	INCREASE IN YIELD DUE TO PHOSPHATE	PHOS-PHORUS IN SAND CLAY MIXTURE	PHOS-PHORUS ABSORBED BY PLANTS
			gm.	gm.	mgm.	mgm.
Adsorbed	Montmorillonite	0.002N H₂SO₄	8.27	2.67	14.3	7.8
Adsorbed	Kaolinite	0.002N H₂SO₄	7.47	2.17	14.2	7.0
Adsorbed	Montmorillonite	0.2N HNO₃	8.27	2.67	14.9	6.5
Adsorbed	Kaolinite	0.2N HNO₃	7.33	2.03	16.9	6.4
Adsorbed	Montmorillonite	0.1N NaOH	9.57	3.97	24.2	8.7
Adsorbed	Kaolinite	0.1N NaOH	7.30	2.00	23.4	5.8
Adsorbed	Montmorillonite	Water-alcohol	10.13	4.53	36.9	10.4
Adsorbed	Kaolinite	Water-alcohol	9.50	4.20	33.3	7.9
Soluble	Montmorillonite		8.63	3.03	26.1	9.0
Soluble	Kaolinite		9.13	3.83	26.1	9.7
No phosphate	Montmorillonite		5.60	....	....	3.3
No phosphate	Kaolinite		5.30	....	....	3.7
No fertilizer			2.23	....	....	1.2

* Each result represents an average of three similar pot treatments.
† Dry weight per pot
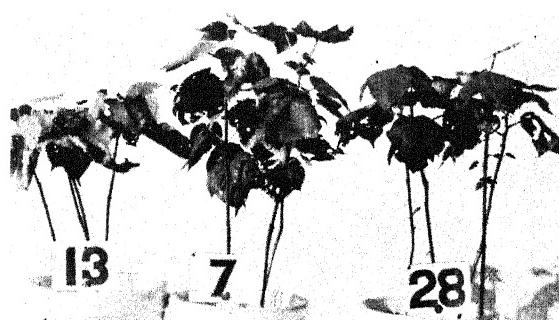
FIG. 2. EFFECT OF ADSORBED PHOSPHATE UPON GROWTH OF COTTON

Pot 13—Sand + kaolinitic clay with no adsorbed phosphorus

Pot 7—Sand + kaolinitic clay with 16.9 mgm. phosphorus adsorbed against 0.2N HNO₃

Pot 28—Sand + kaolinitic clay with 14.2 mgm. phosphorus adsorbed against 0.002N H₂SO₄

grown than on any other treatment. In no case was the extractant solution strong enough to remove all of the phosphate available to the cotton plants.

The data in table 2 also show that the cotton plants utilized large amounts

of the adsorbed phosphates.   In some cases 40 to 50 per cent of the phosphate held by the clay was utilized by the plants.

Comparing the amount of phosphate adsorbed by the clays in tables 1 and 2, one finds a slight difference in the phosphate adsorbed even by the same treatment.   For example, the montmorillonitic clay absorbed 14.3 mgm. phosphorus against the $0.002N$ H_2SO_4 extractant in table 2, compared with only 11.4 mgm. in table 1.   In one case the extracting solution may have remained in contact with the clay longer, but in every case an attempt was made to treat all the clays as described by the methods used.   The montmorillonitic clay adsorbed 35.9 mgm. against $0.1N$ NaOH in table 1, in comparison with only 24.2 mgm. in table 2.   In this case the larger amounts of phosphate adsorbed in table 1 are due to the fact that this clay remained in contact with the soil 3 months instead of the usual 48 hours.   This shows that the longer the phosphate remains in contact with the soil, the more strongly it is held.   Its availability to oats, however, was not decreased by such a treatment.

<div align="center">DISCUSSION</div>

The results with both oats and cotton show that these plants can utilize large amounts of adsorbed phosphate that cannot be removed by the extractant solutions commonly used.   These results suggest that much of the phosphate adsorbed by soils can be used efficiently by certain plants, and that large amounts of phosphate heretofore considered fixed are available to plants.

In an earlier study (3) it was found that cotton grew well on soils low in readily available phosphate (Truog method) and that it failed to respond to applied phosphate on many soils even though the readily available phosphate of the soil was increased.   By utilizing large amounts of adsorbed phosphate already present in the soil, cotton and oats may be able to grow well on many soils that contain very little readily available phosphate, as determined by the common methods.

Throughout the cotton belt, complete fertilizers high in phosphate are used annually, and since only small amounts of phosphate are removed in the harvested cotton, large reserves of adsorbed phosphate may accumulate in the soil. If the adsorbed phosphate in the soil can be utilized, the high phosphate content of many complete fertilizers can probably be reduced economically.   In Mississippi, many field experiments with cotton show that even where soils respond well to phosphate, complete fertilizers with 4 per cent P_2O_5 are as good as those containing 8 and 12 per cent P_2O_5.   It is believed that until the nitrogen content of Mississippi soils is increased many plants will not respond to high rates of phosphate.

The results obtained in this study also suggest that the common methods of determining readily available phosphate do not remove all of the phosphate that is available to cotton and oats.

The results show that cotton and oats utilized the adsorbed phosphate whether it was held by kaolinitic or montmorillonitic clay.   Most of the fine clays, in the soils of the Coastal Plain region probably consist largely of one of these types,

and since the clay fraction is primarily responsible for phosphate fixation, phosphorus applied to Coastal Plain soils should be adsorbed in a manner similar to that adsorbed in these experiments.

SUMMARY

The ability of oats and cotton to feed on adsorbed phosphates was determined by growing these plants in pots containing sand supplied with a nutrient solution but with only that phosphate which had been adsorbed by the clay against acid and alkaline extracting solutions. Both kaolinitic and montmorillonitic clays were used to adsorb a known amount of phosphate, and the relative value of the adsorbed phosphate was measured both by crop yields and by the amount of phosphate absorbed by the plants. The results show that cotton and oats grew well on relatively small amounts of adsorbed phosphate whether it was held by the kaolinitic or the montmorillonitic clay, and that the plants utilized a large percentage of the adsorbed phosphate present.

Of the methods studied, Truog's was the most effective in removing the readily available phosphate from the clays, but even it failed to remove large amounts of phosphate that were available to the plants.

The results indicate that much of the phosphate adsorbed by the soil can be utilized efficiently by certain plants, and that large amounts of phosphate that heretofore have been considered fixed are available to plants. If the cotton and oat plants can utilize adsorbed phosphate efficiently, the high phosphate content of many fertilizers can be reduced economically, especially on soils that have previously received large phosphate applications.

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AVAILABILITY OF ADSORBED IONS TO PLANTS GROWING IN QUARTZ SAND SUBSTRATE[1]

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It has been shown[2] that when potassium, calcium, and magnesium permutites and nitric, sulfuric, and phosphoric acid aniline blacks[3] are suspended in water, solutions of ions that will support the growth of plants are produced. The present paper reports experiments which show that when the adsorption complexes are mixed with quartz sand and the whole mass is adjusted to an adequate moisture content, the adsorbed ions become available and support growth.

SOLUTIONS AND METHODS

The four-salt mixture described by Hartwell *et al.*[4] for growing plants in solution was reduced to three salts by eliminating monocalcium phosphate, and the proportion of calcium nitrate was increased so that the calcium content remained equivalent to that in the original solution. This change results in an increase in nitrate and a decrease in phosphate, while all the other essential ions remain the same. The cation and the anion (as acid) content in milliequivalents per liter are as follows:

K	0.80	HNO_3	3.46
Ca	3.46	H_2SO_4	1.60
Mg	1.60	H_3PO_4	2.40

These quantities are found in a liter of solution containing 0.0008 M KH_2PO_4, 0.00173 M $Ca(NO_3)_2 \cdot 4H_2O$, and 0.0008 M $MgSO_4 \cdot 7H_2O$. A mixture containing these amounts is taken as one unit. In the experiments described, multiples and fractions of this unit are used.

Glazed crocks of 3-liter capacity were fitted at the base with rubber stoppers containing bent glass tubes so that the water level in each pot could easily be determined. Washed beach pebbles were placed in the crocks to a depth of 2 inches and above this, 2 liters of quartz sand containing various amounts of salts or adsorbed ions. Iron and microelements were added at weekly intervals. The amount of water in each pot was kept at a predetermined level by additions through a glass tube immersed in the sand and pebbles so that it rested slightly above the bottom of the crock.

EXPERIMENTAL

In order to compare the availability of adsorbed essential elements and soluble salts containing these elements, when mixed with quartz sand, two series of crocks each containing 2 liters of sand were prepared. Each pot contained one unit of combined nitrogen, sulfur, and phosphorus (as acid) per liter of sand and either one unit of adsorbed cations (P1) or a fraction thereof plus cation chlorides (CCl) to make one unit of cations (figs. 1 and 2).

Geneva red kidney beans and Manchu soybeans were planted, one and five seeds per pot, respectively. No growth data were taken, but figures 1 and 6
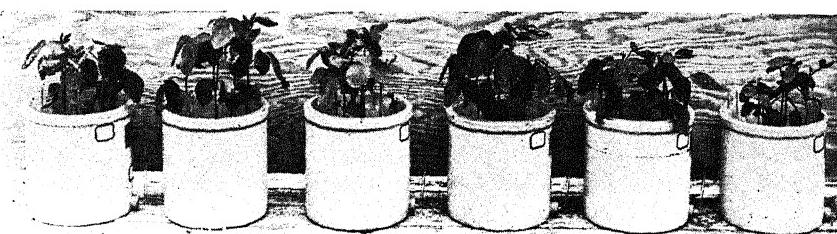
FIG. 1. GROWTH OF SOYBEANS IN QUARTZ SAND SUPPLIED WITH ESSENTIAL ELEMENTS IN THE FORM OF IONS ADSORBED ON ANILINE BLACK AND IN THE FORM OF SOLUBLE SALTS

Pot treatments, left to right—D1 P1; D1 P$\frac{1}{2}$ CCl$\frac{1}{2}$; D1 P$\frac{1}{4}$ CCl$\frac{3}{4}$; D1 CCl1; 1 MgSO$_4$, Ca(NO$_3$)$_2$, KH$_2$PO$_4$; Check. D1 is equivalent to 1 unit of anions (as acid), adsorbed on aniline black; P1, 1 unit of adsorbed cations; CCl1, 1 unit of cation chloride per liter of sand.

FIG. 2. GROWTH OF KIDNEY BEANS IN QUARTZ SAND WITH MIXTURES DESIGNATED IN FIGURE 1

show that in general the pots containing adsorbed ions, as a whole or in part, supported better plant growth than those pots containing soluble salts.

A second experiment was established to ascertain the duration of the fertilizer-supplying power of the adsorption complexes. Two series of nine pots were used. Each pot was prepared in the manner previously described, except that crock 2 contained 2 liters of fine sandy loam of moderate fertility instead of quartz sand. The crocks contained the following ingredients: crock 1, 0 adsorbed units per liter; crock 2, 0 units; crock 3, 4 units; crock 4, 3 units; crock 5, 2 units; crock 6, 1 unit; crock 7, $\frac{1}{2}$ unit; crock 8, $\frac{1}{4}$ unit; crock 9, $\frac{1}{8}$ unit.
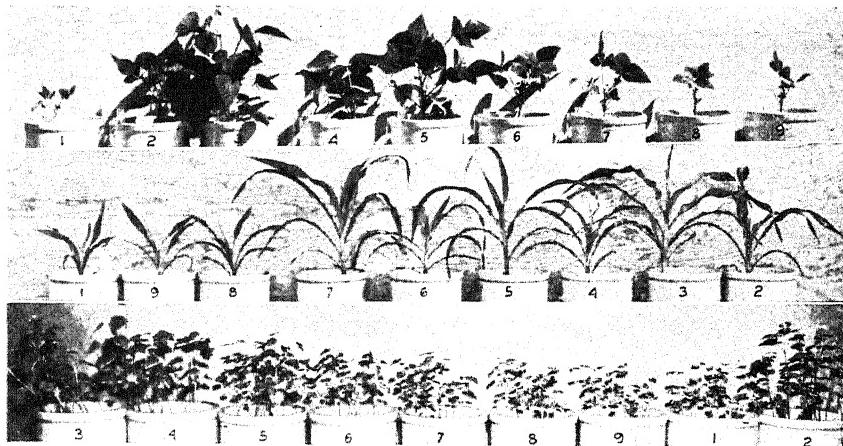
FIG. 3. GROWTH OF PLANTS IN SERIES 1—CROP SUCCESSION, KIDNEY BEANS, CORN, AND BUCKWHEAT

Crock 1, check, no adsorption units per liter; crock 2, soil; crock 3, 4 units; crock 4, 3 units; crock 5, 2 units; crock 6, 1 unit; crock 7, ½ unit; crock 8, ¼ unit; crock 9, ⅛ unit.
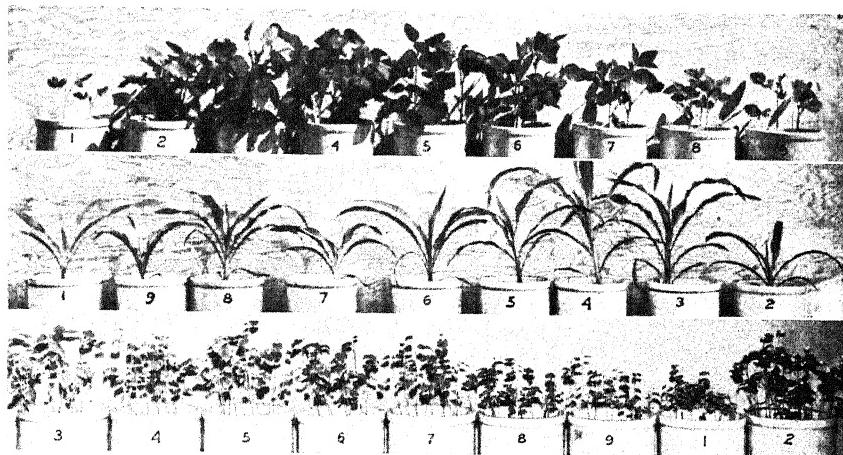
FIG. 4. GROWTH OF PLANTS IN SERIES 2—CROP SUCCESSION, SOYBEANS, CORN, AND BUCKWHEAT

Crocks 1–9, as in figure 3
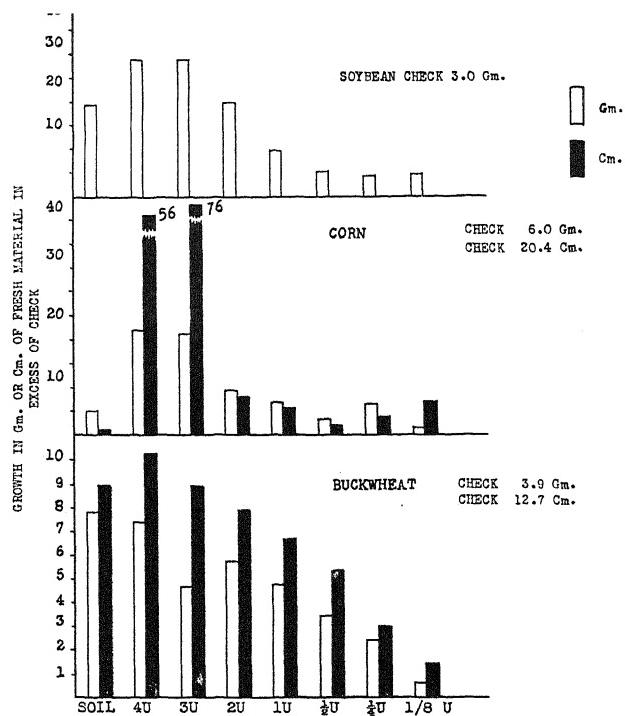
FIG. 5. GROWTH RESPONSE OF KIDNEY BEAN, CORN, AND BUCKWHEAT TO FERTILIZATION—
SERIES 1—EXPERIMENT 2
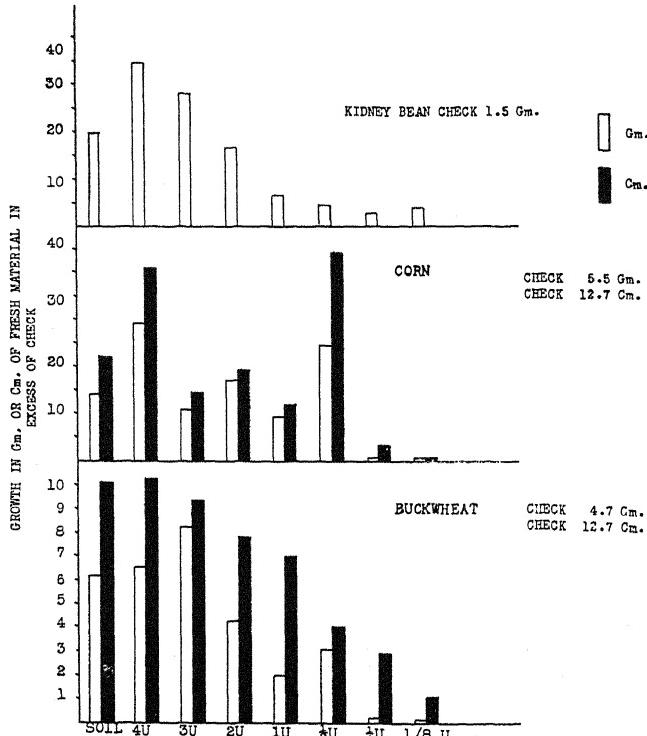
FIG. 6. GROWTH RESPONSE OF SOYBEAN, CORN, AND BUCKWHEAT TO FERTILIZATION—
SERIES 2. EXPERIMENT 2

Three crops were grown in succession: series 1, kidney bean, flint corn, and buckwheat; series 2, soybeans, flint corn, and buckwheat. The growth data are summarized in figures 3 to 6.

DISCUSSION

In almost all cases, plant response to fertilization, when based on either fresh weight or height of plant, is parallel to the quantity of ions supplied (figs. 5 and 6). There is, however, an interplay between the 4 and 3 units, so that in some instances the former shows a greater yield of fresh weight whereas the latter shows a greater height of plant. This situation can be reversed, however, as seen for buckwheat in series 1.

The only extensive irregularity is in series 1 when corn was used. This discrepancy can be explained by the chance inclusion of heterogeneous seed, for the growth of corn in series 2 parallels fertilization.

It is quite possible to evaluate soil fertility in terms of adsorbed ions. Excluding the corn experiment in series 1, the fresh weight of plant tissue from soil is equivalent, in three instances, to the average obtained in the 2- and 3-unit pots, containing adsorption complexes. In the remaining two cases soil yields are equivalent to 4 units and 1 unit. An average of these values indicates that the fertility of the soil used in this experiment is equivalent to that found in approximately 2.5 units of adsorbed ions when mixed with quartz sand and kept at an adequate moisture content. Height measurements can also be used, and the average unit giving growth equivalent to soil is 2.7. In these experiments, however, height measurements were more variable than weight values.

SUMMARY

The essential fertilizer ions adsorbed on either permutite or aniline black, when mixed with quartz sand, will support plant growth. A comparison of equal amounts of soluble salts and adsorbed ions shows that the adsorbed ions produce greater plant growth. In general, crop yields, whether measured in terms of fresh weight or height, parallel fertilization.

DETERMINATION OF ACTIVE MANGANESE IN SOIL[1]

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During the last decade considerable attention has been given to the measurement in soil of the manganese that can be utilized by plants. Piper (2) pointed out the unique property of soil manganese to reflect with rapidity the oxidation-reduction condition of the soil. He concluded that the manganese in soil exists in an oxidation-reduction equilibrium and contended that the amount of manganous manganese in the soil gives information as to the ability of the soil to provide the plant with the required manganese.

In 1935, Leeper (1) maintained that the supply of manganous manganese is not always a good criterion of available manganese, as some soils cannot maintain a satisfactory level of this form of manganese. His work showed that a measurement of manganese within the manganous-manganic equilibrium in the soil is a more reliable indication of the capacity of the soil to provide the plant with the required manganese. He proposed the hypothesis of the existence of soil manganese in a dynamic oxidation-reduction equilibrium, which may be expressed as follows: (*a*) Water-soluble $Mn^{++} \leftrightarrows$ (*b*) exchangeable $Mn^{++} \leftrightarrows$ (*c*) easily reducible $MnO_2 \leftrightarrows$ relatively inert manganic oxides. The easily reducible manganese dioxide would include compounds of every combining proportion from MnO to MnO_2. The composition of these manganic compounds is not constant but may be conventionally written as the dioxide, MnO_2.

The first three members of this equilibrium represent the active manganese, which indicates its availability to the plant. Leeper considered the quantity of easily reducible manganese dioxide to be of major importance. He found that any soil having less than 15 p.p.m. of easily reducible manganese dioxide would be deficient in manganese for plant growth. A soil having more than 100 p.p.m. of easily reducible manganese dioxide would contain a very ample supply of manganese. By using the procedure described, it has been possible for investigators to identify the manganese-deficient soils that have a neutral to alkaline reaction in Michigan (3) and in Australia (1).

A procedure, which is a modification of Leeper's, has been developed by the writers and applied with success. This procedure, which follows, will identify:

1. Manganese-deficient neutral and alkaline soils.
2. Strongly acid soils that will become manganese-deficient when limed to near neutrality.
3. Soils that are likely to contain such excessive quantities of available manganese as to be toxic to plants.

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[1] The investigation reported in this paper is in connection with a project of the Kentucky Agricultural Experiment Station and is published by permission of the director.

PROCEDURE

The procedure is designed to measure the three forms of active manganese in the soil; namely, that which is soluble in water; that which takes part in the cation-exchange phenomena; and that which exists as easily reducible manganese dioxide. In this procedure, a fresh moist sample of soil is extracted successively with distilled water, with a neutral normal solution of ammonium acetate, and with a neutral normal ammonium acetate solution containing 0.2 per cent of hydroquinone. Results are expressed as parts of Mn per million of the dry soil. Details of the procedure are as follows:

Water-soluble manganese. To 25 gm. of soil in a 500-ml. Erlenmeyer flask add 250 ml. of distilled water, stopper the flask tightly, and shake in a machine for 30 minutes. Filter the mixture through a Büchner funnel. If the filtrate is not clear, refilter it through a layer of acid-washed asbestos in a Gooch crucible. Evaporate the filtrate to dryness, dissolve the residue in $(1+4)$ H_2SO_4, and to destroy organic matter boil the solution until fumes of SO_3 are evolved. Determine manganese in this solution by the method described by Willard and Greathouse (4). Return the soil and the asbestos filter pad to the original flask for the determination of exchangeable manganese.

Exchangeable manganese. Add 250 ml. of a normal ammonium acetate solution adjusted to pH 7.0. Stopper the flask and shake it in a machine for 30 minutes or allow it to stand for at least 6 hours with frequent shaking. Filter the mixture through a Büchner funnel, evaporate the filtrate to dryness, and destroy the acetates by heating in the beaker over an open flame. Dissolve the residue in $(1+4)$ HNO_3, and determine manganese as directed for the water-soluble form. Avoid the use of H_2SO_4 at this point in soils having a high content of exchangeable calcium. Return the soil to the original flask for the determination of easily reducible manganic compounds.

Easily reducible manganese dioxide. Add 250 ml. of a neutral normal ammonium acetate solution containing 0.2 per cent of hydroquinone to the flask containing the soil from which the water-soluble and the exchangeable manganese have been removed, shake it at frequent intervals for at least 6 hours to ensure complete reduction, and filter through a Büchner funnel. Add 10 ml. of $(1 + 1)$ H_2SO_4 and 10 ml. of concentrated HNO_3 to the filtrate and evaporate to a small volume, and finally to dryness, by gently heating over a burner. Dissolve the residue in $(1 + 4)$ H_2SO_4 and determine the manganese as directed for the water-soluble form.

APPLICATION OF THE PROCEDURE

The procedure can be used to identify manganese-deficient soils that are slightly acid to alkaline in reaction (3). In these soils the trend of the manganous-manganic system is strongly toward manganic manganese. Only a trace of water-soluble manganese and 2 to 5 p.p.m. of exchangeable manganese are found in such soils. If these soils have less than 25 p.p.m. of easily reducible manganese dioxide they will not supply plants with sufficient manganese for

normal growth. Productive soils of this group usually contain 100 or more p.p.m. of easily reducible manganese dioxide.

Strongly acid leached soils are usually very low in active manganese. In their natural acid condition, however, they are able to provide the plant with

TABLE 1

Active manganese in acid, neutral, and alkaline soils and its relation to manganese needs and toxicity

Mn in p.p.m. of air-dry soil

SOURCE OF SOIL SAMPLES	SOIL pH	WATER-SOLU-BLE Mn^{++}	EX-CHANGE-ABLE Mn^{++}	REDUCI-BLE MnO$_2$ AS Mn^{++}	RELATIVE SUPPLY OF Mn FOR PLANTS
Neutral and alkaline soils					
1. Berea College garden, Kentucky	7.6	0.0	4.5	26.8	Deficient
2. Muck soil, Michigan (3)	7.4	0.2	1.6	15.0	Deficient
3. Sand Gap Ridge, Kentucky	7.4	0.0	4.0	339.0	Ample
4. Maury silt loam, Kentucky	6.8	0.0	3.0	541.0	Ample
Strongly acid soils					
5. Eroded subsurface soil, Adair Co., Kentucky	5.1	0.0	1.0	2.1	Deficient when limed
6. Subsurface soil, Sand Gap, Kentucky	4.9	0.0	1.2	0.8	Deficient when limed
7. Eroded subsurface soil, Larue Co., Kentucky	5.2	0.0	2.8	114.8	Not deficient when limed
8. Subsurface soil—well drained, Green Co., Kentucky	5.3	0.8	7.8	114.8	Not deficient when limed
Soils fertilized with manganese					
9. Subsurface soil—river alluvium, Green Co., Kentucky, + 200 p.p.m. Mn	5.2	65.0	82.0	960.0	Toxic amount probable
10. Near Berea experiment field, Kentucky, + 200 p.p.m. Mn	4.8	12.8	59.8	189.9	Toxic amount probable
11. Muck Soil, Michigan (3), + 250 p.p.m. Mn	7.5	0.4	10.7	111.5	Satisfactory
12. Berea College garden, Kentucky, + 200 p.p.m. Mn	7.6	0.2	3.2	102.1	Satisfactory

ample manganese to maintain growth (1). The trend of the manganous-manganic system in these soils is strongly toward the manganous forms (3). This provides a small but constant supply of available manganese for the plant. When such soils are limed to a neutral or alkaline reaction the trend of the manganous-manganic system is reversed and the supply of manganese to the plant becomes inadequate. Leeper (1) concluded from his work that

heavy application of lime to a strongly acid soil containing less than 25 p.p.m. of easily reducible manganese dioxide is likely to cause manganese deficiency. In clay soils this quantity must be very low before overliming injury will be produced. Under Kentucky conditions the quantity can be as low as 10 p.p.m. before overliming will be evident. Overliming injuries have been produced on soils from Adair and Jackson Counties which show 0.0 and 2.8 p.p.m. of easily reducible manganese dioxide.

Manganese toxicity in a soil can be predicted by using this procedure. If soluble manganese is added to a soil it will be fixed in most well-aerated soils by oxidation to manganic manganese. If a soil is unable to fix the soluble manganese, the trend of the manganous-manganic system is strongly toward the manganous form. If much manganous manganese is present in the soil, manganese toxicity to plants will occur when reducing conditions exist. The measurement of the water-soluble, the exchangeable manganese, and the easily reducible manganese in a soil which has recently received an application of manganous manganese will give a picture of the trend of the manganous-manganic system. A normal well-aerated soil will show 90 per cent of its active manganese as easily reducible manganese dioxide. A soil which does not readily oxidize the manganese will have considerable quantities of water-soluble and exchangeable manganese.

Table 1 shows the active manganese content of certain Kentucky and other soils. Previous experience (3) has shown that the Berea College garden soil as well as the alkaline Michigan muck soil will give an increased crop growth with an application of manganese. The soils from Sand Gap and Maury silt loam will not show any benefit from applications of manganese.

The subsurface soils from Adair County and Sand Gap will show a depression in plant growth when limed to an alkaline pH. The very similar soils from Larue and Green Counties will not show this depression. The easily reducible manganese dioxide in the Larue County soil is 115 p.p.m. against 2.1 for the Adair County soil.

Soils 9 to 12 in table 1 show the difference in the capacity of the soil to fix added manganese. The Berea College garden and the Michigan muck soils rapidly oxidize the added manganese to the manganic form. This oxidation is very slow in the Green County soil and in that taken near the Berea experimental field. These two soils would thus be likely to show easily soluble manganese in toxic amounts under reducing conditions.

CONCLUSIONS

The active manganese in the soil includes the readily available manganous manganese and the easily reducible manganic manganese. The manganous-manganic manganese exists in an oxidation-reduction equilibrium reflecting the state of oxidation of the soil.

The status of the manganous-manganic manganese equilibrium can be established by a measurement of the active manganese. A procedure is described for the measurement of the three forms of manganese constituting the active

manganese; namely, that which is soluble in water; that which takes part in the cation-exchange phenomena; and that which exists as easily reducible manganese dioxide. The forms of active manganese are determined in the leachates from successive extractions of the soil with distilled water, neutral normal ammonium acetate, and neutral normal ammonium acetate solution containing 0.2 per cent hydroquinone.

The procedure described for determining the active manganese will identify:

Neutral to alkaline soils that are manganese-deficient for plant growth. A soil of this type having less than 25 p.p.m. of easily reducible manganic oxides is likely to be deficient.

Strongly acid soils that will become manganese-deficient with liming. Strongly acid soils having less than 25 p.p.m. of active manganese are likely to become manganese-deficient when limed.

Soils with high and low capacity to oxidize added manganese salts. In general, manganese-deficient soils have a high capacity for the oxidation of added manganese.

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MECHANISM OF WATER ATTACK ON DRY COHESIVE SOIL SYSTEMS

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The attack of dry cohesive soils by free water is of great importance in agriculture and in soil engineering. The consequences of such attack are known to vary considerably for different cohesive soils even though the dimensions of the samples and the environmental conditions are identical. The behavior of a soil system toward water appears, therefore, to depend mainly on the properties of the constituents and on the structural characteristics of the system under consideration. Minor, but still important, factors are the temperature and the viscosity of the water and, to some extent, the atmospheric pressure. Other factors are concerned with the shape and the dimensions of the cohesive system. The phenomena actually occurring in the field are functions of the particular group of acting determinant factors. Thus, in one case, the action of the water may result in a progressive liberation of particles from the surface of the system, with or without subsequent removal of these particles; in another case, a general penetration and saturation of the system by water may take place, resulting in a shear failure or a mud flow. Because of the great variability of the extrinsic factors that are able to influence the observable results of water attack, these results themselves evidently are of infinite variability. It is believed, however, that the extrinsic factors may easily be evaluated for specific cases after the general theory of the mechanism of water attack has been established and correlated with intrinsic soil properties. The present work is offered as a contribution toward an understanding of the functional connection of soil physical properties with the type of phenomena observed in attack by water.

HYPOTHETICAL MECHANISM OF WATER ATTACK

An air-dry cohesive soil system represents a structure composed of soil particles that are held together by adhesive films. The cementing power of these films is a function of their own physical and chemical characteristics and of the particles that they hold together. More specifically, the cementing principle may be: (a) the surface tension of the soil moisture; (b) chains of oriented dipoles linking a positive charge on one particle with a negative one of the neighboring particle or *vice versa;* (c) formation of an electric field by ions dissociated from the particles and by water dipoles, the field being shared by the surfaces of two or more particles; (d) a special cementing agent such as calcium carbonate, hydrous

oxides of iron and aluminum, and organic matter. These cements may represent reversibily or irreversibly coagulated colloids and may, therefore, induce permanent or only temporary cohesion.

If a cohesive soil system is exposed to free water, the affinity for water of the internal soil surface will cause the water to move into the system as a consequence of the existing energy potential. (If this energy potential is small or nil as a result of saturation of the soil with water, then the effect of free water on the system is also small or nonexistent.) If the affinity of the soil particles for water is greater than that for the cementing film, or as the surfaces of such films are obliterated, the structure loses its cohesion, and the liberated particles separate from the system. In accordance with this concept, two phenomena must be considered and analyzed: first, the penetration of the water into the soil system; and second, the action of the water on the cementing films, resulting in a lowering and possible destruction of the cohesion of the system.

The relative speed with which water penetrates into a soil system is of maximal importance in connection with the type of physical changes to be expected and also with the rapidity of these changes. The speed of penetration is directly proportional to the affinity of the internal surface for water, which may be called the "capillary head," and to the fourth power of the effective radius of the pores. Therefore, if two soil systems of equal size and of equal pore volume possess different effective capillary radii, the ratio of their speeds of water penetration will be that of the fourth powers of their radii, and the ratio of the amounts of water passing through a certain layer will be proportional to that of the squares of their radii. If the internal soil surface is able to immobilize proximal water layers by adsorption, the effective pore radii are accordingly reduced. Resisting the penetration of the water is its viscosity, which is a function of its temperature, of the amount and kind of solutes it contains, and of its proximity to water-fixing soil surfaces. Resisting are also the free air of the soil pores and the air previously adsorbed by the internal soil surface but liberated by the entering water. If the air can move out of the system freely, its resistance is comparatively small because of its small coefficient of internal friction as compared with that of water. If the air becomes entrapped, however, its pressure is increased proportionally with the decrease of available volume Accordingly, pressure of sufficient magnitude may be built up to expand or even to burst the soil system after its cohesion has been sufficiently decreased by the action of the penetrating water. Whether or not this latter reaction occurs depends upon the speed and extent of obliteration of the cohesive forces by the action of water. Obviously, the following cases may be differentiated as typical consequences of water attack on dry cohesive soil systems:

I. Speed of bond destruction equal to or greater than that of water penetration. This condition results in a progressive orderly slaking of soil particles or soil aggregates.

II. Speed of bond destruction less than that of water penetration, with sufficient air vents to prevent building up of gas pressure. This condition results either in no failure of the system, or in failure after a prolonged period of total saturation with water. In this case the type of failure depends on the test method used; however, in all cases the resulting fragments of the system are relatively large and few in number.

III. Speed of bond destruction less than that of water penetration, with conditions favorable to the entrapping of air. This condition results in the building up of air pressure leading to bursting of the soil system after the cohesional forces have been reduced, by the action of the water, to a level below the pressure of the entrapped air.

Though these are the basic types of soil failure occurring as a result of water attack, combined and intermediate types must logically be expected with actual soils.

AVAILABLE METHODS FOR THE STUDY OF WATER ATTACKS

A number of methods have been developed to study the effect of water on dry cohesive soil systems. A few of these, which are illustrative of the general testing principles employed, are described below.

In the original procedure of the Public Roads Administration (4, pp. 378–379) dried cylindrical soil specimens 1 inch in diameter and 1 inch high are placed on a brass ring attached to a supporting device and are completely immersed in water. The time in minutes required for the specimen to disintegrate sufficiently to fall through the ring is taken as the slaking value. More recently a coarse screen has been substituted for the brass ring.

In another method used by this agency the soil specimen is suspended and partly immersed in water, the latter being in a container placed on a platform of a balance. The rate of disintegration is determined by the time required for a given percentage of the specimen to be deposited in the container.

The Public Roads Administration also has employed a method which was originally used by Russian pedologists. In this method the specimen is formed in a mold used to make tensile test specimens for cement mortar. After drying, the specimen is coated by means of paraffin with exception of a center stripe $\frac{1}{4}$ inch wide around its narrow portion. The specimen is then suspended in water and the time necessary for complete separation of the upper and lower part of the specimen is recorded.

Bouyoucos (1) has described a method in which air-dry lumps of soil are placed on a No. 10 sieve and are allowed to slake 24 hours in water. The particle size of the material passing through the No. 10 sieve is determined by wet-sieving through Nos. 20, 40, 60, 80, and 100. The sieves used have openings of 1.98, 0.84, 0.42, 0.25, 0.18, and 0.15 mm. respectively.

Puri (5) has devised a slaking test in which a jet of water is impinged in small droplets on a dumbbell-shaped soil block resting on two glass rods. The type of specimen is the same as that used by the Russian pedologists. The period from the beginning of the experiment to the toppling of the soil specimen is recorded as slaking time.

Eno (3) has reported the use of a field test in which a cylinder of soil approximately 1 inch in diameter and 1 inch high is dried for 48 hours and placed in water of 70°F. The time in minutes required for the cylinder to slake into a conical pile is recorded as the slaking time.

The results of slaking tests have often been used in the study of erosiveness of soils. Methods like those of Bouyoucos or of Boyd (2) have been employed for this purpose. Such use, however, has been limited more or less to consideration

TABLE 1

Physical properties of some natural and homoionic soil materials

	NAT.	H	Na	K	Mg	Ca	Ba	Al	Fe
Putnam subsoil									
Liquid limit......	35	35	48	37	39	38	37	36	36
Plastic limit......	18	19	16	19	17	17	18	21	20
Shrinkage limit...	15	18	16	17	16	15	16	18	20
Field moisture equivalent....	23	24	23	21	21	24	25	24	24
Heat of wetting* .	2.8	4.2	3.4	2.1	3.5	2.8	3.5	2.1	3.5
Water intake†	.68	.75	1.23	.70	.82	.80	.78	.60	.74
Percentage of #40 material									
0.05–0.005 mm. .	55	60	42	58	65	59	55	60	52
0.005 mm........	33	31	47	30	26	30	33	29	35
0.001 mm........	12	18	30	12	15	13	16	18	25
Loess pampaneo subsoil‡									
Liquid limit.......	76	56	65	51	63	60	62	60	55
Plastic limit......	31	29	28	31	29	31	28	28	29
Shrinkage limit...	12.8	13.7	13.5	14.9	14	13.4	12.9	12.8	13.3
Field moisture equivalent....	44	41	42	40	42	46	45	45	44
Heat of wetting ..	5.5	3.5	4.8	3.5	4.5	5.5	2.8	5.5	4.8
Water intake	.96	.87	1.35	.89	.89	.87	.88	.87	.84
Marshall subsoil§									
Liquid limit	52	47	69	43	60	53	51	49	44
Plastic limit......	24	26	21	25	24	23	23	28	27
Shrinkage limit...	13.7	18.3	16.7	18.7	15.8	16.9	15.9	18.3	19.7
Field moisture equivalent....	37	40	36	35	38	39	38	43	40
Heat of wetting ..	2.8	5.6	4.9	2.8	5.6	3.5	4.2	5.6	4.9
Water intake	.69	.66	1.08	.59	.82	.78	.71	.74	.62
Loess pampaneo topsoil‖									
Liquid limit	40	36	32		40	41	38	37	36
Plastic limit......	27	30	20		28	29	29	30	30
Shrinkage limit...	21	25	17		23	27	24	27	23
Field moisture equivalent....	33	33	27		33	36	34	34	33
Heat of wetting ..	.69	1.03	1.38		1.05	2.07	.34	.69	0.0
Water intake	.69	.68	.68	.61	.71	.68	.61	.66	.61

* In cal./gm. soil; † In cc./gm. soil (Winterkorn-Baver apparatus).

‡ Percentage of #40 natural soil: 0.05–0.005 mm., 39; 0.005 mm., 50; 0.001 mm., 30.

§ Percentage of #40 natural soil: 0.05–0.005 mm., 55; 0.005 mm., 37; 0.001 mm., 22.

‖ Percentage of #40 natural soil: 0.05–0.005 mm., 53; 0.005 mm., 27; 0.001 mm., 10.

TABLE 1—(*Continued*)

	NAT.	H	Na	K	Mg	Ca	Ba	Al	Fe
*Cecil subsoil***									
Liquid limit	75	76	76	74	78	76	80	69	78
Plastic limit......	38	42	46	36	44	42	44	38	42
Shrinkage limit...	32	30	34	29	30	31	30	29	30
Field moisture equivalent....	41	40	44	42	45	44	40	39	42
Heat of wetting ..	2.02	1.35	1.35	1.35	2.02	2.7	2.7	2.02	1.35
Water intake	.88	.83	.66	.69	.76	.68	.88	.71	.66

** Percentage of ≠40 natural soil: 0.05–0.005 mm., 9; 0.005 mm., 76; 0.001 mm., 62.

of the sizes of the slaking products rather than to the dynamics of the slaking process itself.

EXPERIMENTAL MATERIALS AND METHODS

The soil materials investigated were Putnam, Marshall, Cecil, and loess pampaneo subsoils, and loess pampaneo topsoil. Beside the natural material, the H-, Na-, K-, Mg-, Ca-, Ba-, Al-, and Fe-modifications were employed. The latter were prepared by elutriation with the chlorides of the respective ions.

As a basis for the interpretation of the phenomena occurring in the attack of water on the dry soil specimens, the following soil properties were determined: size composition, liquid limit, plastic limit, shrinkage limit, field moisture equivalent, and heat of wetting. The test data are given in table 1. Standard methods were used for their determination.

The method used to study the effect of water on the dry cohesive soils was that of the Russian pedologists. In preparing the specimens, moisture in amount somewhat above that of the plastic limit was kneaded into the dry soil. An amount of soil equal to the volume of the mold was separated from the mass of the soil, kneaded well to obliterate any streaks, layers, or other inhomogeneity, placed in the mold, and carefully formed to fit the outline of the mold. Sticking of the sample to the mold was prevented by means of paper strips. After removal from the mold, the samples were dried carefully, in order to avoid cracking, in systems with decreasing water vapor pressure. After the weight of the samples attained constancy on continued exposure to the laboratory air, the samples were kept for 2 days over concentrated H_2SO_4. Then they were coated with paraffin, with exception of the $\frac{1}{4}$-inch center stripe, replaced in the desiccator for two more days, and finally were ready for testing. The test consisted in suspending the samples completely in water and observing both the time required for the separation of the lower part of the sample from the upper part and the attendant phenomena. Without the latter, the time data are of very limited value.

The natural soil materials exhibited the following slaking phenomena:

Loess pampaneo subsoil—rapid corrosion and dispersion of the soil system into very finely divided particles;

Putnam subsoil—rapid corrosion and dispersion into small soil aggregates and primary particles;

Marshall subsoil—swelling of the soil system and disintegration into fine soil aggregates and primary particles;

Loess pampaneo topsoil—disintegration into soil aggregates of intermediate size;

Cecil subsoil—clean fracture of lower portion of specimen from upper parts.

In line with the discussion on the hypothetical mechanism of water attack on dry cohesive soil systems, loess pampaneo subsoil and Putnam subsoil exhibit the type represented by case I; Marshall subsoil is an intermediate type between cases II and III; loess pampaneo topsoil and Cecil subsoil exhibit two distinct variations of case II. In accordance with the precepts developed above, the type of slaking encountered is an expression of the relative magnitude of the cohesive forces in the soil system and of the antagonistic effect of the water affinity of its internal surface. On the other hand, the speed of water action is dependent upon the speed of water penetration and upon the time required for marked reduction of the cohesive forces. Therefore, analysis of the mechanism of water attack requires indexes for the cohesive forces in the system, for the water affinity of the internal surface, and for the permeability of the soil at the prevailing pore conditions.

The bulk cohesion in a dry soil system can be easily obtained from an analysis of tensile and compression test data by means of Mohr's circle method. As in the case of metals or of salt crystals, however, the cohesion obtained experimentally is only a fraction of the true molecular or ionic cohesion, because the failure planes follow lines of weakness caused by aggregation of the constituents into secondary units. Cohesion data thus obtained should not be used indiscriminately in the study of molecular phenomena. Also, such data are not representative of the cohesion of the soil in moist conditions. Following a trend of thought previously employed by Terzaghi (6) relative to sedimentation volumes, one might assume that, with soils of comparable size and shape of constituents, the shrinkage limit may be indicative of shear resistance at low moisture contents. Obviously, particles that are strongly bound to one another offer greater resistance to shrinkage than do particles with small attraction for one another. This concept is, of course, only a very qualitative one; however, it is of interest to note from tables 2 to 6 and also from the study of table 1 that for the natural soils the slaking time increases with increasing value of the shrinkage limit.

Another indicator of primary cohesional forces in a soil system is the size of the slaked-off aggregates. Again, hypothesis and test data appear to be in agreement for the natural soils, since the slaking times vary inversely with the size of the slaked particles. It might, therefore, be deduced that the effectiveness of

water attack on dry soil systems is controlled primarily by the cohesive forces exerted by the primary soil units. It appears that aggregation analysis may be employed as a qualitative measurement of the cohesive forces. This fact should be of greatest importance in regard to the basic justification of most of the erosion studies made up to the present time.

Affinity of internal soil surface for water

One might be tempted to assume that the affinity of the internal soil surface for water can be determined easily as the heat of wetting. But heat of wetting determinations are usually made on powdered soil materials; in this condition active spots on the surface of the soil particles, which in the cohesive system are engaged in holding together soil particles, are free to react with the water, producing considerable heat of wetting. For this reason, heat of wetting data obtained on powdered soil material cannot be considered as indicative of the water affinity of strongly aggregated soil systems. On the other hand, if soil clods are used in this test, the liberation of the heat is so slow as to involve considerable heat loss and inaccuracy of the data. For soils with little affinity of the particles for one another and with small tendency to aggregation, however, heat of wetting data appear to be valuable tools if properly used.

Influence of soil permeability

It has been brought out that the speed of water penetration dominates the slaking picture in soil systems in which the speed of bond destruction equals or exceeds that of the penetration. The rate of penetration is proportional, among other factors, to the water affinity of the internal soil surface. On the evidence of such easy destruction of the cohesive bonds between the particles, these bonds must be considered as rather weak. As a consequence, it is very probable that the water affinity of such systems is well indicated by the magnitude of their heat of wetting. Soils of this type suffer most from the attack of water in the field. For this reason, they are deserving of particular attention and consideration in any attempt to explain the difference in the consequences of water attack as a function of intrinsic soil properties. The Putnam soil falls into this category.

Analysis of data on Putnam subsoils

From the behavior of Putnam subsoil during water attack, as shown in table 2, and also from its pedological characteristics, it is evident that the bond between its constituent soil particles is easily destroyed by water. For this reason the slaking behavior of Putnam subsoil can be expected to be mainly a function of the permeability of the soil and of the water affinity of its internal surface. The permeability of a soil is determined by the number of capillaries per unit area and by their average diameter. In connection with another investigation, and with homoionic Putnam soils prepared by neutralization of the H-systems, Winterkorn and Moorman (10) have determined permeabilities for different voids ratios (ratio of void space to volume of solid materials). At a voids ratio of 1.3 the

K-Putnam soil possessed a permeability of $15.9 \cdot 10^{-8}$ cm./second. For theoretical purposes the pore space in the Putnam soil may be substituted by a bundle of

TABLE 2

Slaking behavior of natural and homoionic Putnam subsoils

| IONS | SLAKING TIME | | APPEARANCE OF SPECIMENS |
	Experimental	Calculated	
	Minutes	*Minutes*	
Nat.*	38	38	Small aggregates, some swelling
H	29	28	Small aggregates, much swelling
Na	138†	74	⎫ Very fine dispersion
K	73†	41	⎭
Mg	66	38	⎫
Ca	45	44	⎬ Small aggregates, much swelling
Ba	34	38	⎭
Al	38	37	Large aggregates, flaking
Fe	20	28	Large aggregates, flaking and fracture

* Natural soil.

† These large values are probably due to both single grain structure and osmotic type of swelling.

capillaries of an average diameter. The number of capillaries per square centimeter and their average diameter may be obtained in the following way:

For viscous flow
$$v = \frac{1}{\eta} \frac{\pi r^4}{8l} (p_1 - p_2)t$$
or

$$k = \frac{vl}{p_1 - p_2} \cdot \frac{1}{t} \cdot n_c = \frac{1}{8} \frac{\pi r^4}{\eta} n_c,$$

where

v = volume of water in cc.
η = coefficient of viscosity
π = 3.1416
r = average radius of tube in cm.
l = length of tube in cm.
$p_1 - p_2$ = pressure head in cm. water
t = time in seconds
n = porosity or pore area per sq. cm.
n_c = number of capillaries per sq. cm.
$n = r^2 \pi n_c$
k (exp.) = $15.9 \cdot 10^{-8}$ cm./sec.
η (30°C.) = $0.800 \cdot 10^{-2}$

If we assume η (average) = $2 \times 0.800 \cdot 10^{-2} = 1.6014 \cdot 10^{-2}$ (because of effect of soil on viscosity of water) and substitute into

$$k = \frac{1}{8} r^4 \pi n_c = \frac{1}{8} \frac{n}{\eta} r^2$$

Then we obtain
$$r = \sqrt{\frac{1}{n}8k\eta}$$

$$= \sqrt{\frac{2.3}{1.3} \times 8 \times 15.9 \times 10^{-8} \times 1.6 \times 10^{-2}}$$

$$= 1.885 \cdot 10^{-4}$$

$$n = r^2 \pi n_c = 3.56 \times 3.14 \times 10^{-8} \cdot n_c$$

$$= 0.565$$

$$n_c = \frac{0.565 \times 10^8}{3.56 \times 3.14} = 5.04 \cdot 10^6$$

Therefore, the equivalent capillary system may be pictured as containing 5.04×10^6 capillaries per square centimeter of an average radius of 1.885×10^{-4} cm. If this capillary system is assumed to be equivalent to that of the soil under consideration, the permeability of the system as a function of n^2 can be found as indicated below. For this calculation η (30°C.) is used, since for this purpose the water viscosity is assumed not to be influenced by the capillary wall. Then

$$k = \frac{1}{8}\frac{\pi r^4}{\eta}n_c \quad \text{and since} \quad r^2 \pi n_c = n \quad \text{and} \quad r^2 = \frac{n}{\pi n_c}$$

$$k = \frac{1}{8}\frac{1}{\pi n_c \eta}n^2$$

if

$$\eta = 0.8007 \cdot 10^{-2}$$
$$\pi = 3.14$$
$$n_c = 5.04 \cdot 10^6$$

then

$$k = 0.984 \cdot 10^{-6} \; n^2 \quad \text{or}$$
$$k = 98 \; n^2 \cdot 10^{-8} \; \text{cm./sec.}$$

Figure 1 shows the $k - n^2$ relationship in graphical form. If the experimental data referred to above (10) are inserted in the graph it is evident that from a certain n^2 on, the actual k-values follow a curve parallel to the theoretical. In other words, the k-values follow a relationship:

$$k = 98(n^2 - n^2_s) \; 10^{-8} \; \text{cm./sec.}$$

in which n^2_s is represented by a point on the abscissa at which the latter is cut by the linear extension of the part of the k-curve which is parallel to the theoretical curve. For the homoionic Putnam soils it has been found that, approximately:

$$n_s = 0.009 \times \text{liquid limit.}$$

For the K-Putnams oil the n_s is about 80 per cent of the porosity at the liquid limit. This n_s is therefore a constant for a specific soil containing clay of th expanding lattice type, and may be calculated from the liquid limit. After its determination, the permeability of thoroughly disturbed soil systems of like mechanical analysis, such as the soil for which the relationship was derived, and of the same clay type, may be calculated for different voids ratios. The relationship does not hold for porosities below n_s. This n_s may be called the "limiting or specific porosity" of a wet soil. In accordance with the derivation, the square of the porosity of a soil system minus the square of n_s is an indicator
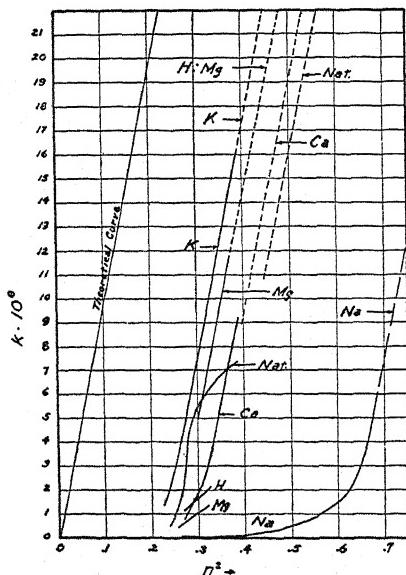
FIG. 1

FIG. 2

FIG. 1. RELATIONSHIP BETWEEN PERMEABILITY AND SECOND POWER OF POROSITY WITH 5.04 MILLION CAPILLARIES PER CUBIC CENTIMETER

FIG. 2. FACTORS INFLUENCING THE SLAKING OF PUTNAM SUBSOILS

of the permeability of the system at the particular state under consideration. The porosity of a soil system at the shrinkage limit may be calculated as follows:

$$n = \frac{\dfrac{\text{shrinkage limit}}{100} \times \text{sp. gr. of soil particles}}{1 + \dfrac{\text{shrinkage limit}}{100} \times \text{sp. gr. of soil particles}}$$

The function $(n^2 - n_s^2)$ is therefore an indicator of the permeability of a soil, especially if this function is positive; if it is negative, swelling of the system may be expected on exposure to water.

Figure 2 shows the slaking times, the permeability indexes $(n^2 - n_s^2)$, and the heat of wetting for the different homoionic Putnam soils. As might be expected, the slaking time tends to decrease with increasing permeability and increasing
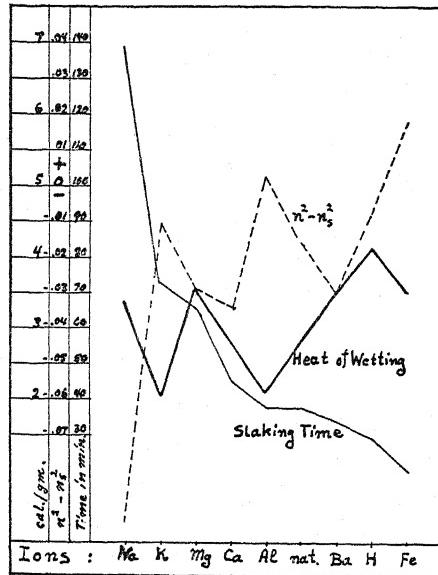
heat of wetting. Maxima in the $(n^2 - n_s^2)$ curve are usually counterbalanced by minima in the heat of wetting curve. That this balance is not 100 per cent may be explained by the fact that the heat of wetting was determined on powdered soil systems. As indicated previously, some of the heat-producing spots on the powdered minerals may be engaged in the cohesive soil system to hold particles together and may, therefore, not be free for energetic water adsorption. For the slaking of the Putnam soils an empirical formula may be written as follows:

$$\text{Slaking time in minutes} = \frac{5{,}300}{100 + 100(n^2 - n_s^2) + 20 \times \text{heat of wetting/gm.}}$$

Data calculated by means of this equation and experimentally obtained values are shown in table 2.

TABLE 3

Slaking behavior of natural and homoionic loess pampaneo subsoils

IONS	SLAKING TIME	H₂O INTAKE	APPEARANCE OF SPECIMENS
	minutes	*cc./gm.*	
Na	28	1.35	⎫
Nat.*	25	0.96	⎪
H	22	0.87	⎪
Fe	15	0.84	⎪
K	14	0.89	⎬ Very fine dispersion in all cases; water muddy
Ca	13	0.87	⎪
Ba	11	0.88	⎪
Mg	10	0.89	⎪
Al	8	0.87	⎭

* Natural soil.

Discussion of slaking behavior of loess pampaneo subsoils

The physicochemical properties of the loess pampaneo soil have been described in previous papers (9). The conclusion reached was that the most important property of the subsoil is its avidity for water. Since the heat of wetting of the homoionic clays is not considerably influenced by ionic substitution, the water avidity appears to be an intrinsic property of the soil constituents.

As far as the slaking behavior of the different ionic soil modifications is concerned, it appears important that: (a) the shrinkage limits are small, suggesting small attractive forces between the particles in the presence of water, a fact borne out by the great dispersion of the slaked particles; (b) the energy of water absorption is not markedly different for the different ionic modifications. As a consequence, there remains as a major variable only the available pore space as expressed by the shrinkage limit and the thickness of the adsorbed water layers. Unfortunately, no permeability data and no permeability–pore-space function, such as those for the Putnam soil, were available for the loess pampaneo. The slaking data for the different homoionic modifications are given in table 3 together with water intake data obtained b̲y̲ ̲_̲_̲_̲_̲ ̲_̲ ̲_̲ ̲_̲

method (7).   These data, however, indicate little more than the fact that a large
but not vehement water sorption, as exemplified by many sodium-systems, tends
to decrease the speed of slaking.

Discussion of slaking behavior of Marshall subsoils

The Marshall subsoil contains a considerable amount of organic matter, and
for this reason it is difficult or impossible to evaluate accurately or even approxi-
mately the heat of wetting data.   In the slaking experiment the Na- and K-soils
showed dispersion into very fine particles, and considerable swelling of the whole
system appeared in the case of the other ionic modifications.   Since the coher-
ency of the system and also the water affinity of the internal soil surface are
largely dominated by the organic films around the soil particles, it is very diffi-
cult to obtain an idea of the level of these forces and their variation in the differ-
ent ionic soils.   It is possible, however, that because of the organic matter,

TABLE 4

Slaking behavior of natural and homoionic Marshall subsoils

IONS	SLAKING TIME		APPEARANCE OF SPECIMENS
	Experimental	Calculated	
	minutes	*minutes*	
Na*	159	31.4	
Nat.†	30.0	29.0	
Al	26.8	20.3	
Mg	26.0	28.6	Dispersion, water muddy. Much swelling, water
Ba	24.4	24.6	clear
Ca	20.6	24.0	
H	19.2	19.4	
K	17.2	17.3	Dispersion, water muddy, much swelling
Fe	17.0	16.9	

* Large value probably due to osmotic swelling.
† Natural soil.

these forces do not vary much for the different ionic modifications.   If this be
the case, then it should be possible to express the slaking time as a function of
the liquid limit, as indicative of the water-binding ability, and of the shrinkage
limit, as indicative of the accessibility to penetration.   Table 4 contains the
slaking data for the Marshall soils as determined by experiment and as calcu-
lated by means of an empirical formula:

$$\text{Slaking time (in min.)} = 7.6 \frac{\text{liquid limit}}{\text{shrinkage limit}}$$

With exception of the Na- and Al- soils, this formula appears to hold within
the limits of accuracy of the experimental data.   The great difference between
actual and calculated swelling time of the Na-soil may be due to the fact that the
procedure for the determination of the liquid limit is too rigorous to permit the

measurement of the osmotic type of swelling that is known to occur with mono-valent exchange ions, in addition to the hydration swelling (8). The deviation in the case of the Al-soil may point to a better cementing effect of the Al-organic film than that obtained for the other organic films.

Discussion of slaking behavior of loess pampaneo topsoils

It has been noticed in a previous study (9) that the dominant factor of the loess pampaneo topsoil is its elasticity and resiliency caused by the amount and type of organic matter present. This resiliency of the soil is reduced by treat-ment with Na ions. As a result of the resiliency of the soil the shrinkage limit gives no clue to the adhesive forces acting between the soil constituents. Also, the presence of the organic matter in considerable amounts renders heat of wetting data erratic and of little analytical value. The liquid limit data may be an expression of the resilience of the soil in wet condition rather than an indi-cation of its water affinity. Similar considerations hold for all other physical

TABLE 5

Slaking behavior of natural and homoionic loess pampaneo topsoils

IONS	SLAKING TIME	APPEARANCE OF SPECIMENS
	minutes	
Na	266+	
K	209+	Separation of aggregates and some swelling
Nat.*	49	
Al	33	Parts of specimen flake off
Ba	25	
Ca	20	Separation of aggregates
H	13	Sample breaks straight across
Mg	10	
Fe	6	Separation of aggregates

* Natural soil.

properties tested. The data on the slaking of the natural and homoionic loess pampaneo topsoils are given in table 5. It appears that the physical data available are affected by so many uncertain factors that none of the attempted correlations was considered worthy of presentation.

Discussion of slaking behavior of Cecil subsoil

The Cecil soils resisted the action of water longer than any of the other soils. When failure occurred it was usually a clean separation of the bottom part of the sample from the top part. In consideration of this type of failure and of the time required for it, the latter may be considered as representing the period necessary for a sufficient lowering of the cohesion of the soil to be overcome by the weight of the lower part of the specimen. It stands to reason that the water affinity of the soil should be directly related to the time required for the critical lowering of the cohesion. Unfortunately, it appears difficult to judge the water

affinity of the Cecil soils. The heat of wetting is relatively small; and, because of the low base-exchange capacity of the Cecil soil, variations caused by pulverizing may be expected to be in the same order of magnitude as changes caused by ionic substitution. Because of the porous nature, the mica content, and the lateritic clay type of the Cecil soil, the liquid limits do not seem to be as indicative of the water affinity as they are in the podzolic soils. The slaking data of the Cecil soils are, furthermore, susceptible to great variations, if the preparation of the specimens varies to the slightest extent. The data for the Cecil soils are given in table 6. As for the Argentina topsoil, the available data for the Cecil soils do not quite allow the drawing of definite conclusions on the factors affecting the decrease of cohesion due to water attack.

TABLE 6

Slaking behavior of natural and homoionic Cecil subsoils

IONS	SLAKING TIME	APPEARANCE OF SPECIMENS
	minutes	
H	360+	
Al	335	
Nat.*	328+	
Ca	245+	
Ba	245+	Lower portions break clean from top portions of specimens
Fe	245+	
Na	229+	
K	213	
Mg	188	

* Natural soil.

SUMMARY AND CONCLUSIONS

The mechanism of water attack on dry cohesive soil systems has been analyzed theoretically and on the basis of data obtained on five natural soils and on a number of their homoionic modifications. Two main factors appear to govern the consequences of the water attack; namely, the driving force or the affinity of the internal soil surface for water, and the cohesive forces holding the system together. The relative magnitude of these forces determines the general reaction picture. On the other hand, the speed with which the particular reaction occurs depends to a great extent on the permeability of the soil system and on the ease with which free and adsorbed gases may escape from the pore space. If this escape is prevented, a type of failure may occur which possesses great similarity to an explosion, although, of course, not liberating so high an amount of energy as is usually associated with this term. The concept that the driving force is the affinity of the internal surface for water makes it easy to understand why certain moist cohesive soil systems may be exposed to free water for any length of time without observable change. It is obvious that the affinity for water is satisfied in such systems and that no driving force for the water attack is left.

The experimental data obtained appear to substantiate the developed theory as far as the erosive soils are concerned. As to the nonerosive soils, it must be admitted that the experimental techniques available at present do not furnish all the information necessary for testing the theory, but no fundamental reasons why the general theory, as developed in this paper, should not hold for all types of cohesive soils appear to exist.

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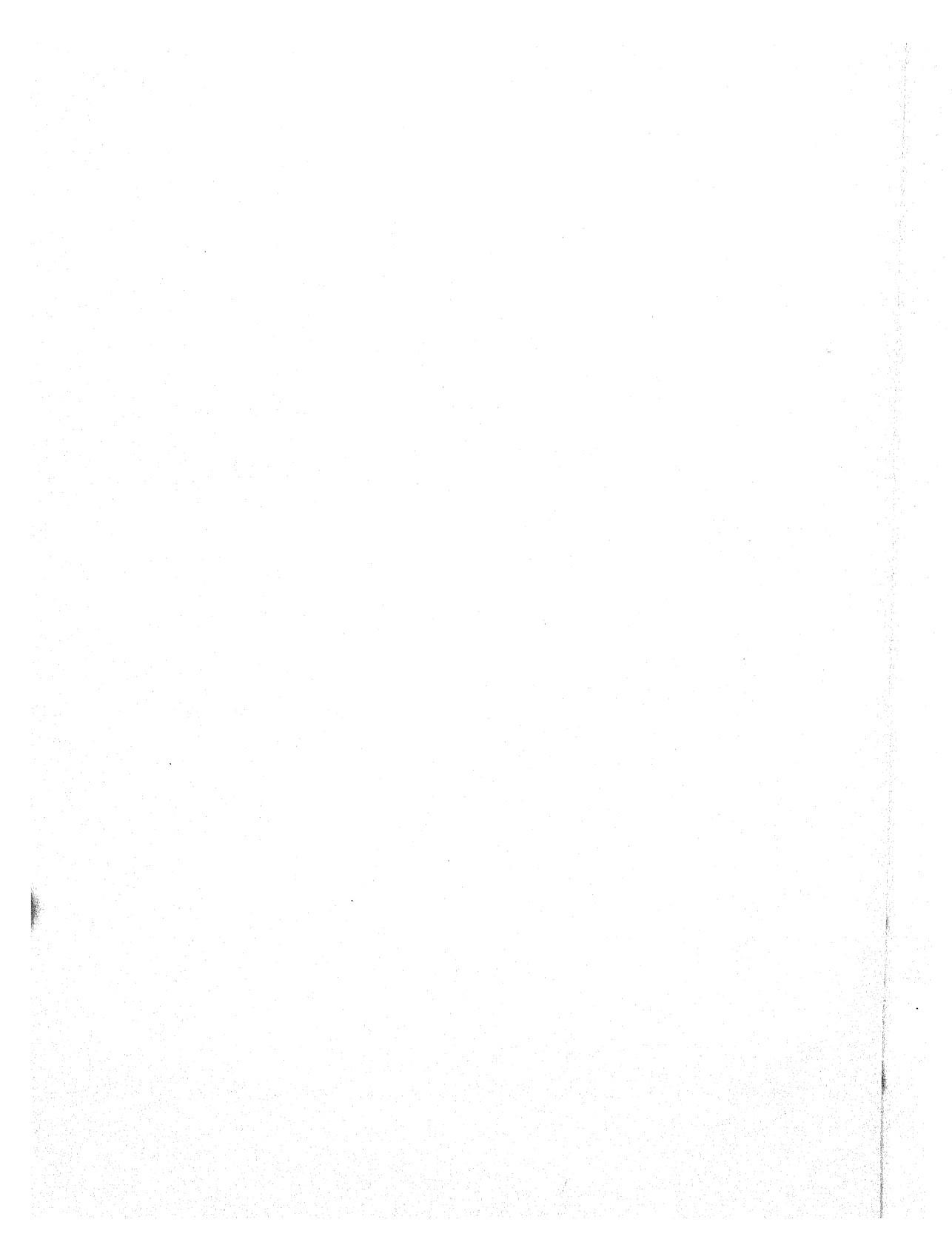
FIELD STUDY OF RESPONSE OF THE ELECTRICAL RESISTANCE OF 2- AND 4-ELECTRODE PLASTER OF PARIS BLOCKS TO VARIATIONS IN SOIL MOISTURE

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An earlier publication,[1] reporting laboratory studies, gave the reasons for comparing the 2-electrode plaster of paris block[2] with the 4-electrode block of the same material. The reproducibility of the contact resistance in the 2-electrode block was so close, apparently, that little could be gained by using the 4-electrode block in preference to the 2-electrode block.

The question of lag[3] in response of the block to changes of soil-moisture content was also considered. When no plants were growing on the soil in which the blocks were placed, the lag was found to be very great at the lower range of soil-moisture content readily available to plants. Where plants were growing on the soil, however, there was no appreciable lag; the roots dried the soil out at the block-soil boundary to the same degree as elsewhere in the soil mass permeated by the roots. With wide differences in the rates of transpiration, it was found, in the laboratory studies, that both the 2- and the 4- electrode plaster of paris blocks gave good reproductions of the same resistance-soil-moisture-content curve during different cycles.[4] If, then, there was any lag in response of the blocks to changes of soil-moisture content, it was not appreciable.

Laboratory studies, however, do not constitute a sufficient basis for recommendations for field practice. In the growing season of 1942, accordingly, field trials were conducted on four plots on which sugar beets were growing and on one plot on which sudan grass was growing. The plots were about 100 feet square. Dikes were put up around the edge so that the irrigation inside the plot could be regulated to give the desired conditions for experimental work. The blocks were placed 18 and 42 inches below the surface of the soil, three at each depth of the plot.

In the laboratory studies an effort was made to provide as many cycles as possible and thereby get as much evidence as was obtainable on the ability of the blocks to repeat, during the different cycles, a given value of resistance when

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[1] Anderson, A. B. C., and Edlefsen, N. E. 1942 Laboratory study of the response of 2- and 4-electrode plaster of paris blocks as soil-moisture content indicators. *Soil Sci.* 53: 413–428.

[2] Bouyoucos, G. J., and Mick, A. H. 1940 An electrical resistance method for the continuous measurement of soil moisture under field conditions. *Mich. Agr. Exp. Sta. Tech. Bul.* 172: 1–38.

[3] Time required for the moisture content of the block to come to equilibrium with the soil.

[4] Changes in moisture conditions commencing with the wetting of the soil by an irrigation and ending with the soil dried out to the permanent wilting percentage.

the soil in which they were placed reached the given moisture content. Obviously, under field conditions, because of the larger amount of soil into which the plants could grow, it was not feasible to have as many cycles during the lifetime of the plants as in the laboratory. Three cycles, could, however, be obtained in some of the plots and two in others for the blocks at the 18-inch depth. Since the soil at the 42-inch depth was dried to the permanent wilting percentage in only one case, the results are not complete at that depth. Of the extensive data obtained in the field studies, results are presented for only the blocks at the 18-inch depth in one soil, of which the moisture equivalent is 29.59 per cent and the permanent wilting percentage 17.87 per cent. The results for other soils of widely different texture show equally good agreement.

Figure 1 presents complete results for the three 2-electrode blocks at the 18-inch level in Yolo clay loam. The graphs to the left show the resistance and the moisture content as a function of time. Irrigations are indicated by the abrupt changes in the moisture-content curves from a low value to a high value with increasing time. The resistance also changes, during an irrigation, from a high value to a low one. A larger number of cycles were obtained in the sandy soils than in the others, obviously because this type of soil can hold much less available water than the other types. All the readily available water in the sandy soils was accordingly extracted from the second-foot depth sooner than in the other soils.

To test the ability of the blocks to replicate values, the resistance has been plotted as a function of moisture content. The results for the two cycles available for each of the three blocks, as shown to the right of figure 1, are quite satisfactory.

Figure 2 shows the results of the 4-electrode blocks plotted in the same manner as those for the 2-electrode blocks. The ability to replicate values seems to be of approximately the same order as that for the 2-electrode blocks. The results with the 4-electrode blocks in the field, just as in the laboratory studies, seem to have no advantage over the 2-electrode blocks. Since much more material is required to construct the 4-electrode blocks and more time is needed to make the measurements, there seems to be no justification for using them in preference to the 2-electrode blocks.

In a few instances among the data obtained on other soils, a considerable discrepancy was noted between the curve corresponding to the first cycle and those corresponding to later cycles, all of which agreed. The reason, doubtless, is that the blocks had not been placed in the soil soon enough and that, therefore, the roots of the actively transpiring sugar beets had not yet had time to permeate the region of soil immediately surrounding the blocks. This region accordingly remained moist while the rest of the soil was being dried out.

From results both in the laboratory and in the field, it is concluded that at field capacity and higher moisture contents, for all the soils studied, the resistances of the 2-electrode blocks are nearly constant, having a value between 400 and 600 ohms, whereas the resistances when all the readily available moisture is used are in the neighborhood of 500,000 ohms. In other words, the blocks
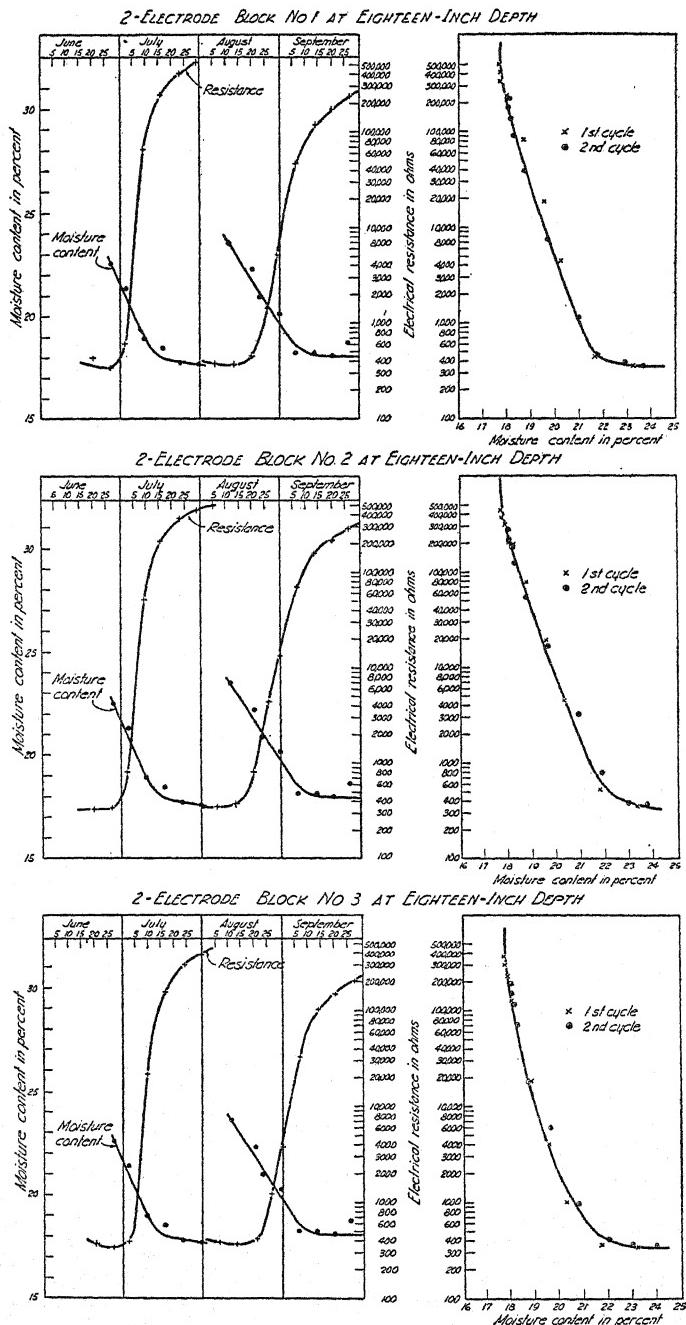
FIG. 1. CURVES SHOWING MOISTURE CONTENT OF YOLO CLAY LOAM AS A FUNCTION OF
TIME, AND ELECTRICAL RESISTANCE OF 2-ELECTRODE BLOCKS AS A FUNCTION OF TIME,
TOGETHER WITH THE DERIVED CURVES SHOWING THE RESISTANCE AS A FUNCTION OF
MOISTURE CONTENT, FOR THREE PLASTER-OF-PARIS BLOCKS AT THE 18-INCH DEPTH
UNDER FIELD CONDITIONS
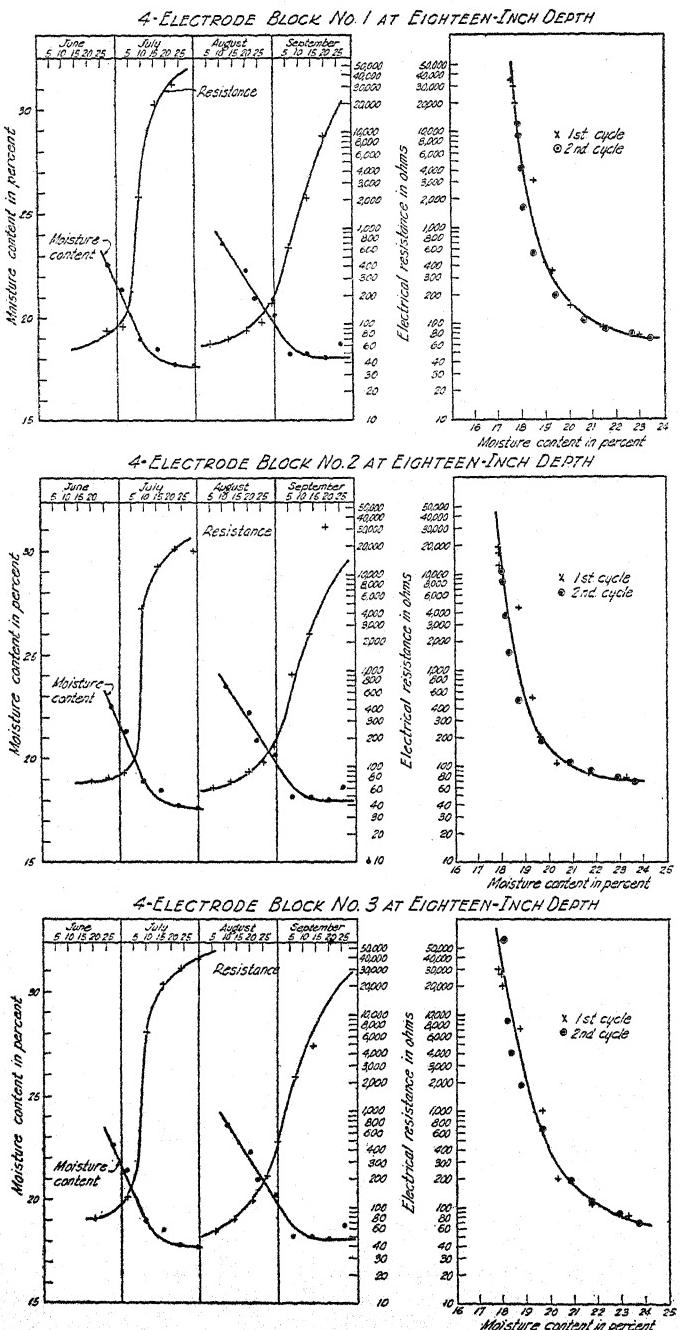
FIG. 2. CURVES SHOWING MOISTURE CONTENT OF YOLO CLAY LOAM AS A FUNCTION OF
TIME, AND ELECTRICAL RESISTANCE OF 4-ELECTRODE BLOCKS AS A FUNCTION OF TIME,
TOGETHER WITH THE DERIVED CURVES SHOWING THE RESISTANCE AS A FUNCTION OF
MOISTURE CONTENT, FOR THREE PLASTER-OF-PARIS BLOCKS AT THE 18-INCH DEPTH
UNDER FIELD CONDITIONS

have approximately the same resistance, in the different soils studied, when all the readily available moisture has been used and also have approximately the same resistances at the moisture equivalent in these soils. This situation was to be expected, inasmuch as the resistance of the block, in the soil of a given salinity, is believed to be a measure of the free energy of the water.

The fact that the blocks, in all the soils tested, have approximately the same resistances at the permanent wilting percentage, makes them especially useful as indicators of need for irrigation. As will be noted from the figures, the resistance increases very rapidly with changes in moisture content in the neighborhood of the permanent wilting percentage. A knowledge of the manner in which the resistance increases as the moisture content decreases and hence as time progresses makes it possible, therefore, for the operator to anticipate the nearness of the permanent wilting percentage. For field practice, it is suggested that a resistance of the block of about 10,000 ohms is a warning that the moisture of the soil in contact with the block is almost depleted. At this resistance some moisture is still available, the amount depending on the soil. The block, if placed at shallow depths may, of course, reach this resistance long before the beets or almost any other crop will show need for irrigation, because the roots in most cases would have available water at lower depths. As experiments show, most crops seem to grow normally as long as there is readily available water in the root zone. At the upper levels of the root zone, accordingly, these blocks may indicate that the permanent wilting percentage has been reached even though some water may still be available at greater depths. A safety factor can therefore be obtained by regulating the depth at which the block is placed.

All these studies were carried out on fertile alluvial soils of the alkaline rather than the acid type, with average salt content. The tests were confined to soils of the Yolo series covering a wide range of texture, soils that constitute a fairly high percentage of the fertile soils of the interior valleys of California. The conclusions here drawn are not necessarily valid, therefore, under all other conditions. For the soils studied, however, the 2-electrode blocks are fairly reliable guides for irrigation practice, but further tests should be made before these blocks can be recommended for general use on all soils.
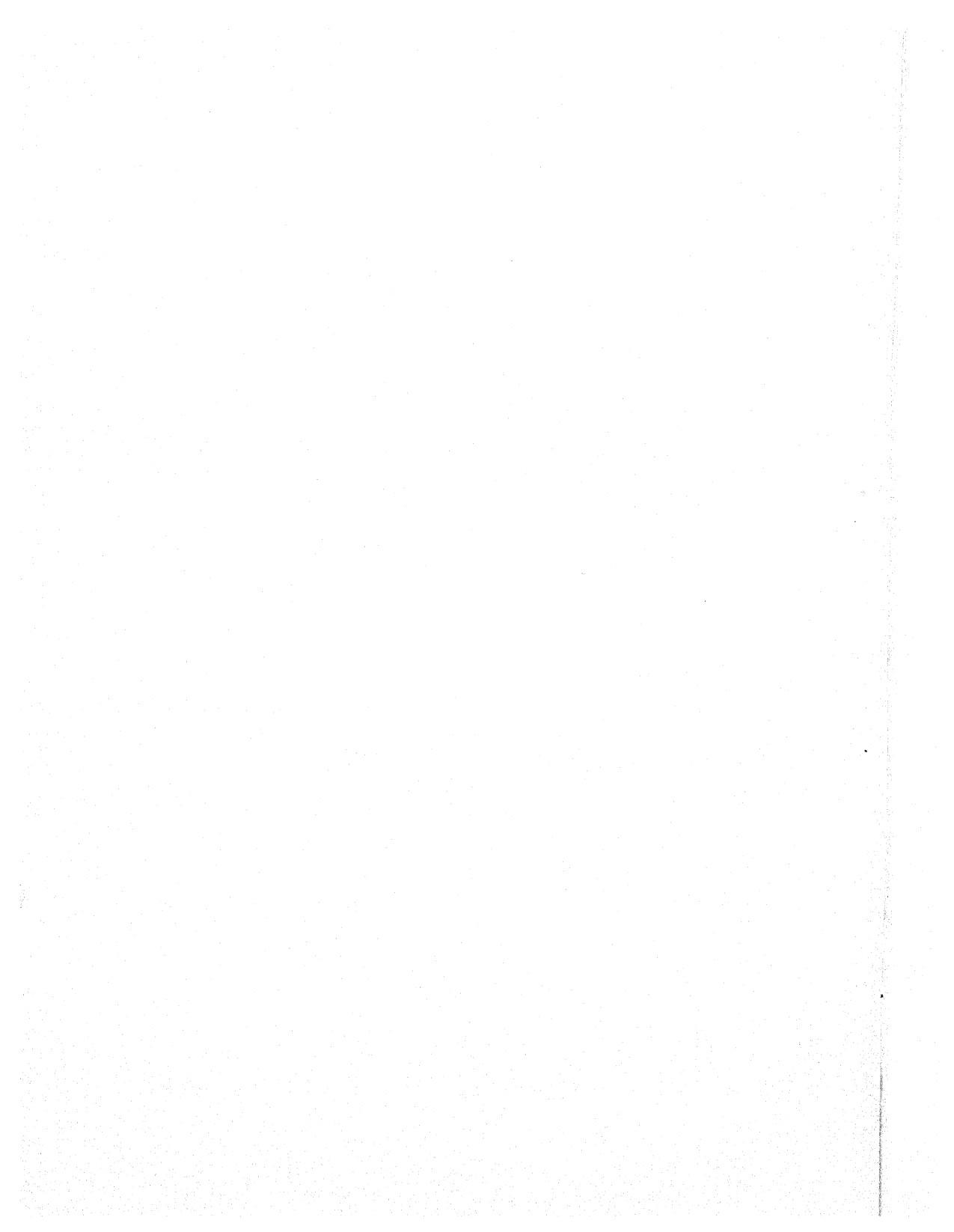
DISTRIBUTION OF ANTAGONISTIC ACTINOMYCETES IN NATURE[1]

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HISTORICAL

The ability to antagonize various bacteria and fungi is widely distributed among actinomycetes. This property is not limited to any one constituent group of these microorganisms, but is known to be characteristic of the various genera into which the actinomycetes have recently been classified (18).

Gasperini (3) is credited with being the first to demonstrate the antagonistic action of certain actinomycetes. He reported that "Streptothrix develops habitually in a spontaneous manner upon the surface of bacteria and fungi, upon which it lives to a limited extent in the form of a parasite, due to the faculty that its mycelium possesses to digest the membrane from these lower fungi." Greig-Smith (6) demonstrated that soil actinomycetes are able to antagonize not only bacteria, but also certain fungi. Since actinomycetes grow only slowly in natural soils, the possibility was suggested that they constitute an important factor limiting bacterial development. Lieske (9, pp. 138–143) has shown that certain actinomycetes are able to bring about lysis of many dead bacteria. They were also found to antagonize the growth of various bacteria, this process being selective in nature, affecting only certain organisms, such as *Staphylococcus aureus*.

Rosenthal (11) isolated a strain of an *Actinomyces* that brought about the lysis of the diphtheria organism. Gratia and Dath were primarily interested in an *Actinomyces* species that could lyse dead cells of staphylococci and of other bacteria. Later, living bacteria were also found to be attacked (4, 5). This type of bacteriolytic activity was studied in detail by Welsch (22, 23), and the active culture filtrate was designated as "actinomycetin."

Borodulina (2) demonstrated that actinomycetes are able to antagonize various spore-forming bacteria and bring about the lysis of the living cells of these organisms. The production of a thermostable active substance on agar media was established; an alkaline reaction reduced the action of this substance, whereas an acid reaction favored it.

According to Krassilnikov and Koreniako (7), many species of true actinomycetes, but not of proactinomycetes, produce a substance that is strongly bactericidal to a variety of organisms. This substance was said to be particularly active against proactinomycetes, mycobacteria, and micrococci. It was less active upon sporeforming bacteria, and had no action at all on nonspore-

forming bacteria. Under the influence of this bactericidal factor, the microbial cells were either entirely lysed or were killed without subsequent lysis. The action upon sporebearing bacteria was bacteriostatic rather than bactericidal. Nonsporeforming bacteria, including species of *Rhizobium* and *Azotobacter*, were not affected at all by this substance, since they were actually able to develop in the filtrates of the antagonists.

Nakhimovskaia (10) made a survey of the distribution of antagonistic actinomycetes in nature and found them to be of wide occurrence. Out of 80 cultures isolated from a variety of soils, 47 possessed antagonistic properties, but only 27 liberated active substances into the medium. These substances possessed the property of inhibiting the growth of gram-positive bacteria, but not of gram-negative bacteria or fungi. The antagonistic effects of actinomycetes were manifested not only in artificial media, but also in soil (10), the interrelations here being much more complex, however. Some of the strains that behaved as antagonists on artificial nutrient media were ineffective under soil conditions. The antagonistic action was found to be more intense in light or podzol soils and much weaker in heavy or chernozem soils. The high content of organic matter in the heavier soils was believed to be one of the factors that resulted in a decrease in the antagonistic activities of these organisms. This was confirmed by adding peptone to a light soil, which resulted in a considerable reduction in the antagonistic action. When, however, the actinomycetes were allowed to multiply in the soil before inoculation with bacteria, such as *Bacillus mycoides*, the antagonism was very pronounced even in the presence of a high concentration of peptone.

An attempt to isolate an antibiotic substance of the type studied by the Russian investigators (2, 7, 10) was made by Kriss (8). He came to the conclusion that this substance, produced by *Actinomyces violaceus*, could possibly be classified with lysozyme. It was insoluble in ether, petroleum ether, benzol, and chloroform and was resistant to the action of light, air, and high temperatures. The optimum reaction for the production of this active substance was found to be pH 7.1–7.8. The activity could not be increased by selective cultivation. Comparison of the properties of this Actinomyces "lysozyme" with those of egg-white lysozyme, convinces one that the two substances are not the same. Although no other active substance was isolated by the Russian investigators, differences in the action of the various antagonistic actinomycetes that they studied point definitely to the fact that the active principles produced by the various organisms are chemically and biologically distinct.

Actinomycetes also possess antagonistic activities against fungi (12, 16, 17). *A. albus* was found (1) capable of inhibiting the growth of ten species of fungi, tested in pure culture. The test fungus was inoculated 5 days after the *Actinomyces*, on maltose agar adjusted to pH 7.4. This effect was shown to be due to the production of an antibiotic substance. A survey of the antagonistic activities of 80 type cultures of actinomycetes, using *Colletotrichum gloesporioides* as the test organism, gave the following distribution of the cultures: 17.5 per cent were strong inhibitors, 38.8 per cent were weak inhibitors, and 43.7 per cent had no inhibiting effect.

Waksman and Woodruff (15, 19) isolated from the soil a pigment-producing *Actinomyces* possessing strong antagonistic properties against bacteria and fungi. This organism was described as *A. antibioticus*, and the active principle, *actinomycin*, was isolated and purified. This substance was not only highly bacteriostatic (especially to gram-positive bacteria) and fungistatic, but was also extremely toxic to laboratory animals. Another active antagonistic organism was later isolated (20), which was found to be a strain of *A. lavendulae*. This organism produced a totally different type of antimicrobial substance, since it was much more active against gram-negative bacteria than were other anti-biotic substances of microbial origin previously reported. This substance was purified and concentrated. It was designated as *streptothricin*.

The antagonistic properties of actinomycetes are not limited to members of the genus *Actinomyces*. A culture of a *Proactinomyces* isolated by Professor Gardner at Oxford, England, as an air contaminant, was found to produce antagonistic effects against a variety of gram-positive bacteria. The active substance pro-duced by this organism was designated as *proactinomycin*. Finally, a represent-ative of another genus, namely *Micromonospora*, was reported by one of us (24) as capable of exerting antagonistic effects against certain bacteria.

This brief review definitely establishes the fact that antagonistic properties are widely distributed among actinomycetes and that the antibiotic substances pro-duced by these organisms vary greatly in chemical nature and in biological activity.

EXPERIMENTAL

The investigations presented in this paper have been carried out with a view to determining, first, how widely distributed are antagonistic properties among actinomycetes; second, what is the specific nature of the antagonistic organisms; and third, what is the nature of the active, or antibiotic, substance produced by the specific antagonists. A fourth aspect of this problem, namely, the sig-nificance of these properties in regulating the microbiological population of soils, composts, and other natural substrates in which actinomycetes occur, is left for a later study.

Occurrence of antagonistic actinomycetes

A systematic survey was first undertaken of the distribution of antagonistic actinomycetes in soils and in composts. This survey was carried out on a group of cultures freshly isolated from the natural substrates and by the use of a collec-tion of cultures taken from the type cultures kept in the laboratory. The first group comprised 244 cultures isolated at random from different soils by the use of the agar plate method.

Since *Bacillus subtilis* was found (21) to be highly sensitive to the action of various antibiotic substances, especially those produced by actinomycetes, it was used as the chief test organism for differentiating the antagonistic properties of the group as a whole. The method of determining the capacity of all the strains to exert antagonistic effects was carried out as follows: An aqueous suspension of

each culture was streaked across the diameter of a Petri dish containing 10 ml. of solidified nutrient agar. The plates were incubated for 48 hours at 28°C., and were then cross-streaked with a fresh aqueous suspension of *B. subtilis*. Those cultures which possessed antagonistic properties showed a clear zone, varying greatly in width, between the growth of the *Actinomyces* and that of the test bacterium.

On the basis of their antagonistic action against *B. subtilis*, as well as other bacteria, the 244 cultures were divided into four groups, as shown in table 1. The first group, comprising 49 cultures or 20 per cent of the total, was highly antagonistic; groups II and III, 57 cultures or 23 per cent, showed some antagonistic properties; group IV, 138 cultures or 57 per cent, possessed no an-

TABLE 1

Distribution of antagonistic actinomycetes in nature

SOURCE OF ORGANISMS	NUMBER OF CULTURES ISOLATED	GROUP I*		GROUP II		GROUP III		GROUP IV	
		Cultures	Per cent of total	Cultures	Per cent of total	Cultures	Per cent of total	Cultures	Per cent of total
Fertile, manured, and limed soil	74	20	27.0	5	6.8	1	1.3	48	64.9
Infertile, unmanured, limed soil	75	11	14.7	8	10.7	4	5.2	52	69.3
Potted soil	13	1	7.7	1	7.7	0	0	11	84.6
Potted soil, enriched with E. coli	21	1	4.8	4	19.0	4	19.0	12	57.2
Potted soil, enriched with mixtures of bacteria	15	12	80.0	2	13.3	0	0	1	6.7
Lake mud	9	3	33.3	4	44.4	0	0	2	22.2
Stable-manure compost	37	1	2.7	20	54.0	4	10.8	12	32.4
Total	244	49	20.1	44	18.0	13	5.3	138	56.6

* The organisms in group I were the most active antagonists; those in groups II and III had more limited antagonistic properties; and those in group IV showed no antibacterial effects with the methods used.

tagonistic action at all. It is of particular interest to note that in a soil enriched with mixed cultures of living bacteria, as many as 80 per cent of the colonies were antagonistic. Not many actinomycetes developed in a soil enriched with *Escherichia coli*, since only very few species are able to antagonize this bacterium.

Thirty-one cultures, selected from group I in this study, were utilized for a further investigation of the active antibiotic principle involved. Against *B. subtilis*, they gave a zone of inhibition greater than 7 mm. on the streak plate test. The cultures were grown in an agar medium containing 1 per cent starch and 0.5 per cent tryptone, for 9 to 10 days at 28°C. They were then extracted with water and filtered. The aqueous extract was added, in various amounts, to 10 ml. nutrient agar, and the plates were streaked with suspensions of *B. subtilis*, *E. coli*, and *Sarcina lutea*. Nine of the antagonistic cultures showed activity against *B. subtilis*, seven against *S. lutea*, and only one against *E. coli*.

A somewhat similar distribution of antagonistic properties among actinomycetes was found (24) in a large group of cultures taken from the type culture collection. This included 164 pure type strains, largely members of the genus *Actinomyces*. Only one *Proactinomyces* and one *Micromonospora* were antagonistic. These 164 cultures were also examined for bacteriolytic properties (24), living *S. aureus* being used as the test organism. On this basis, 87 cultures or 53.1 per cent were found to be inactive, 53 cultures or 32.3 per cent were moderately active, and 24 cultures or 14.6 per cent were highly active. It may, therefore, be concluded that bacteriolytic properties are also widespread among the actinomycetes.

The bacteriostatic or growth-inhibiting properties of the soluble products secreted by some of the most active actinomycetes were next examined. The

TABLE 2

Growth inhibition of bacteria by aqueous extracts of cultures of actinomycetes

ORGANISM	LARGEST AMOUNT OF AQUEOUS EXTRACT, IN 10 ML. NUTRIENT-AGAR, WHICH STILL ALLOWS GROWTH OF TEST BACTERIA			
	E. coli	*S. aureus*	*S. lutea*	*B. subtilis*
	ml.	ml.	ml.	ml.
A. antibioticus	>1.0	<0.1	<0.1	<0.1
A. candidus	>1.0	0.3	0.1	0.1
A. lavendulae	0.3	<0.1	<0.1	<0.1
A. roseus	>1.0	>1.0	0.3	0.3
Actinomyces 3442*	>1.0	>1.0	0.3	0.3
Actinomyces 3443*	>1.0	>1.0	0.3	0.3
Actinomyces 3444*	>1.0	>1.0	0.3	0.3
Micromonospora sp.	>1.0	0.1	<0.1	<0.1
P. gardneri	>1.0	0.1	<0.1	<0.1

* Agar-liquefying strains of *A. coelicolor*.

water extracts of the 10-day-old cultures of these organisms, grown on starch-tryptone-agar, were used. Amounts of 1.0, 0.3, and 0.1 ml. of each extract, respectively, were added to 10 ml. of melted and cooled nutrient agar, which was then plated and allowed to solidify. Four test-organisms were streaked on each prepared plate; namely *E. coli*, *S. aureus*, *S. lutea*, and *B. subtilis*. Of the nine cultures thus tested, five were found to be highly active, some of the test organisms being inhibited by the addition of less than 0.1 ml. of the filtrate per 10 ml. of agar medium. Four species were only weakly active, as shown in table 2.

It is now well established that the antibiotic substances of microorganisms are characterized by their selective action against different organisms. That this is true also of antagonistic actinomycetes is illustrated in table 3, which lists the specific properties of several of the actinomycetes studied. The first group comprises those strains which cause, by the cross-streak method above described, a zone of inhibition of *B. subtilis* wider than 10 mm.; the second group includes strains which, under similar conditions, result in a zone of inhibition less than 10 mm. The following properties were considered for each strain: lytic activit~

TABLE 3

Distribution of bacteriolytic and bacteriostatic properties among species of actinomycetes

ORGANISMS	BACTERIOLYSIS BY LIVING ORGANISMS*	BACTERIOLYSIS BY BROTH FILTRATE†	BACTERIOSTASIS OF B. SUBTILIS BY AQUEOUS EXTRACTS
Group I. Actinomycetes highly bacteriostatic to B. subtilis			
A. antibioticus..	0	—	++
A. californicus..	+	c	0
A. candidus...	++	C, S	++
A. cellulosae...	+	c	0
A. griseus (3326b)......................................	+	c	0
A. lavendulae...	+	c	++
A. reticuli...	+	c	0
A. roseus..	+	C	+
A. ruber..	+	—	0
A. saprophyticus.......................................	++	C, S	0
A. scabies (3031)......................................	+	c	0
Actinomyces sp. (3069).................................	++	c	0
A. albus (G)..	++	C, S	0
Actinomyces sp. (3387).................................	++	C, S	0
P. gardneri...	0	c	++
Micromonospora sp......................................	0	—	++
Group II. Actinomycetes moderately bacteriostatic to B. subtilis			
A. albus (3361)..	++	C, S	0
A. cretaceus...	+	c	0
A. albus, var. ochraleuceus............................	++	C, S	0
A. annulatus..	+	—	0
A. aureus...	+	c	0
A. bovis..	+	c	0
A. fradii...	++	C, S	0
A. griseus..	++	C, S	0
A. halstedii..	+	c	0
A. hominis..	++	C, S	0
A. lipmanii...	+	c	0
A. microflavus..	+	c	0
A. odorifer...	++	—	0
A. praecox..	+	c	0
A. rutgersensis.......................................	++	C, S	0
A. sampsonii..	++	C, S	0
A. scabies (3352).....................................	+	—	0
A. scabies (3021).....................................	++	C	0
A. setonii...	++	C, S	0
A. tetanusemus..	++	C, S	0
A. coelicolor (3033)..................................	+		
Actinomyces sp. (Lieske, No. 23)......................	++	C, S	0
Actinomyces sp. (Lieske, No. 25a)....................	++	C	0

* 0, no action against *S. aureus*; +, moderately active; ++ highly active.

† C and c, lysis of heat-killed *E. coli;* S, lysis of living *S. aureus;* capital letter indicates high activity, small letter moderate activity; —, no activity.

of the growing *Actinomyces* culture on living *S. aureus*; ability of the sterile culture filtrate to lyse heat-killed *E. coli* and living *S. aureus*; ability of sterile extracts of the culture to inhibit the growth of *B. subtilis*. The results presented in table 3 show definitely that different antagonistic organisms found among the actinomycetes possess totally different antibiotic mechanisms, in regard to both the nature of the bacteria acted upon and the mechanism of this action. Several of these organisms have been studied in detail. Some have been well described and some only insufficiently studied. Some mechanisms are well recognized and the active substances have been isolated or at least concentrated, whereas others are merely outlined briefly.

Description of certain antagonistic actinomycetes

The following cultures of actinomycetes have been recognized as possessing important antagonistic mechanisms:

Actinomyces antibioticus Waksman and Woodruff. This organism was isolated (16) from the soil. It was found to produce a highly powerful bacteriostatic substance, designated as "actinomycin" and described in detail elsewhere (19). Out of nearly 400 cultures of actinomycetes thus far tested for antagonistic properties, no other one was found to produce a substance comparable to it in activity, although in a few cases a similar type of action, to a much more limited extent, was indicated.

Actinomyces lavendulae Waksman and Curtis. This antagonistic organism was freshly isolated from the soil, by the use of the bacterial agar plate. This culture differed in certain respects from an earlier description of this organism (13). Hence, it may be designated as a new variety. A brief description of its morphology and cultural characteristics is included here:

Dextrose agar: White, thin surface growth, penetrating deep into the agar medium. Aerial mycelium at first white, later turning a characteristic lavender color. No soluble pigment.

Nutrient agar: Gray, wrinkled growth; scant aerial mycelium produced. Faint brownish soluble pigment. Pigment deep brown on tryptone-agar.

Potato plug: Gray, wrinkled growth, adhering closely to plug, thin mouse-gray aerial mycelium; purple to black pigment of plug in form of zone around growth, later spreading over the whole plug.

Gelatin: Brown to almost black growth, sparse white aerial mycelium on surface in form of ring; medium liquefaction of gelatin; at first no soluble pigment, gelatin later becoming deep brown.

Morphology: Long, straight, little-branched aerial hyphae. No spirals.

Activity: Culture produces a powerful antagonistic substance, designated as "streptothricin" and described elsewhere (20). The influence of nitrogen source on streptothricin production is illustrated in table 4. Certain amino acids appear to be as suitable sources of nitrogen as are proteins and peptones. Further studies brought out the fact that streptothricin can also be produced from pure amino acids, such as asparagine, alanine, and glutamic acid, in the absence of any other carbon and nitrogen source, but not with glycocoll and aspartic acid. In an

amino acid medium, however, on prolonged incubation, an increase in alkalinity results in the destruction of the streptothricin.

Actinomyces albus Krainsky. This organism was isolated in 1936 from the air of the laboratory, at Liége, Belgium, by Welsch (22). Plates of water-agar, containing a suspension of live *S. aureus*, were exposed for half an hour to the air of the laboratory, then incubated at 37°C. for 2 days. Among the few colonies which appeared on the plate was an *Actinomyces* surrounded by a large zone of lysis. The organism was at first designated as *Streptothrix*, and later as *Actinomyces* sp., strain 10. The culture was extensively used in subsequent experiments, and its properties were thought to be very characteristic of all actinomy-

TABLE 4

*Influence of nitrogen source on the bacteriostatic action of filtrate of A. lavendulae**

NITROGEN SOURCE†	SMALLEST AMOUNT OF FILTRATE, IN 10 ML. NUTRIENT-AGAR, INHIBITING GROWTH		
	E. coli	S. lutea	B. subtilis
	ml.	ml.	ml.
Tryptone	0.1	<0.1	<0.1
Tryptose	0.1	<0.1	<0.1
Peptone	1.0	1.0	0.1
Casein	0.3	0.3	<0.1
Egg-albumin	0.3	0.3	<0.1
Asparagine	0.3	0.3	<0.1
Glycocoll	0.3	0.3	<0.1
Alanine	0.3	0.3	<0.1
Aspartic acid	0.3	0.3	<0.1
Glutamic acid	0.3	0.3	<0.1
Phenylalanine	>1.0	>1.0	>1.0
Tryptophane	>1.0	>1.0	>1.0
Tyrosine	>1.0	>1.0	>1.0
NaNO₃	>1.0	>1.0	>1.0
(NH₄)₂SO₄	>1.0	1.0	0.3

* Incubation 7 days.

† Basic medium, 1 per cent glucose, 0.2 per cent K_2HPO_4, 0.2 per cent NaCl, 0.001 per cent $FeSO_4$, 0.25 per cent agar in tap water. Nitrogen source—0.5 per cent.

cetes. This organism is now recognized to be a strain of *Actinomyces albus*. In view of the great heterogeneity of organisms classified as *A. albus*, it has been correlated most closely with the strain of Krainsky, although it differs from it in some respects. It is designated here as the "G strain" in honor of Gratia (24).

The properties of this strain of *A. albus* and the literature pertaining to the subject are reviewed in detail elsewhere (23, 24). The culture dissolves heat-killed gram-negative and gram-positive bacteria, as well as suspensions of living gram-positive bacteria in mineral fluid but not in complex culture media; it has no action on living gram-negative bacteria. It inhibits the growth of many gram-positive bacteria, especially members of the genus *Bacillus*. Culture-filtrates of this organism readily dissolve heat-killed gram-negative and, more slowly, heat-

killed gram-positive organisms. They also dissolve, to a certain extent, suspensions of a few gram-positive living bacteria, namely, *Diplococcus pneumoniae*, *Streptococcus pyogenes*, and some strains of *S. aureus*. Lytic filtrates have been designated as "actinomycetin." They have no bacteriostatic action except after concentration by precipitation with $(NH_4)_2SO_4$. A bactericidal lipoid material was extracted from the filtrates. It was found to originate, in part, from the medium and, in part, from the organism. It is especially active against gram-positive bacteria in mineral suspensions. The group of properties recognized for this organism is frequently found among actinomycetes (24) and may be referred to as antibiotic action of the actinomycetin-type.

A brief description of the cultural and morphological properties of this culture follows:

Nutrient agar: Cream-colored growth with yellowish reverse. Abundant white aerial mycelium with brownish to greenish tinge. No soluble pigment.

Czapek agar: Thin, gray growth, largely in form of individual colonies, which gradually fuse into a mass of growth. Aerial mycelium in form of white concentric zones, very thin and limited, gradually spreading.

Potato plug: Brownish, thin, spreading, lichenoid growth. Powdery chalk-white aerial mycelium appearing in upper part of growth and gradually spreading all over growth. Plug unpigmented.

Milk: Growth in form of cream-colored ring on surface, gradually forming heavy pellicle. White powdery aerial mycelium along edge. Milk gradually peptonizes without previous coagulation. Reaction turns alkaline.

Gelatin: Cream-colored surface growth, thin white aerial mycelium. Rapid liquefaction. No soluble pigment.

Morphology: Growth on Czapek's agar in clumps, with short, straight, branching aerial mycelium, no spirals.

Proactinomyces gardneri Waksman. The growth of this organism upon liquid and upon solid media resembled closely that of typical proactinomycetes. Upon nutrient agar, the growth was soft and elevated, without any aerial mycelium. When this mycelium finally appeared upon dextrose-asparagine-agar, it was slow in developing. In tryptone broth, the growth took the form of small pellets at the base of the flask. Later a thin surface pellicle appeared, resembling bacterial growth, which proved, on microscopic examination, to consist of a branching mycelium. A definite black pigment was slowly produced in the tryptone broth. The specific cultural and morphological characteristics of this organism may be described briefly as follows:

Nutrient agar: Cream-colored, lichenoid growth, no aerial mycelium; very faint brownish pigment.

Dextrose agar: Brownish, lichenoid growth, with wide cream-colored edge; white to grayish aerial mycelium gradually covering surface. Reverse of growth yellowish; no soluble pigment.

Potato plug: Barnacle-like, brownish growth, gradually covering plug; no aerial mycelium. Brownish zone of plug around growth.

Gelatin: Surface, cream-colored ring, no aerial mycelium; green to greenish-

brown soluble pigment gradually diffusing through liquefied portion. Rapid liquefaction of gelatin.

Morphology: The growth on organic media is soft, rather than leathery. There is very little aerial mycelium, except on synthetic media. Sporulation is not that of a member of the genus *Actinomyces* but is characteristic of a *Proactinomyces*.

Activity: The antibiotic substance (proactinomycin) was produced by this organism upon synthetic and organic media. It was primarily active against various gram-positive bacteria. It was soluble in ether, but was different from and far less active than actinomycin.[3]

Micromonospora sp., strain 1. This organism was isolated from lake mud by J. P. Sell. The chief difficulty encountered in the study of the organism was to obtain vigorously growing cultures. In liquid medium, *Micromonospora* does not spread readily, since its mycelium is not easily broken, as is that of members of the genera *Proactinomyces* and *Actinomyces*, and since it sporulates only after a long period of incubation. From a rather poor culture in broth, the growth of the organism was collected by centrifugation, crushed as much as possible with a glass rod, and the suspension spread over the surface of Blake bottles containing 25 ml. of starch-tryptone-agar. A very nearly confluent growth was obtained after 7 days' incubation at 30°C. Fifty milliliters of sterile tapwater was then added to each culture, the bottles were well shaken, and the suspension of the organism was used to inoculate a number of Blake bottles. These cultures showed a confluent growth after 4 days. The procedure was repeated as often as necessary, always with good results.

Micromonospora sp. produces a pinkish-yellow mycelium which, after 3 or more weeks' growth on starch-tryptone-agar, becomes covered with a black, hard crust of spores. After cultivation for 6 or more days, the organism produces a strong fetid odor. Cultures were also made on modified Czapek's agar. The growth was very much slower and poorer, the extracts of the cultures giving no activity. On starch-tryptone-agar, the bacteriostatic activity appears after 2 or 3 days, reaches a maximum in 4 and 8 days, then slowly decreases, but it is still present after 45 days, as shown in table 5.

The antagonistic activity of *Micromonospora* sp. is directed against a number of gram-positive bacteria, the spore-bearing aerobic group being the most susceptible, with the very notable exceptions of *B. mycoides* and *B. cereus*. It is important to note that these two organisms also show, unlike other members of the group, a marked resistance to streptothricin (20). All gram-negative organisms tested were very resistant, as shown in table 6.

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[3] Further details of the cultural characteristics of this organism, the isolation of the active substance, and its activity *in vitro* and *in vivo* will be found in an article by A. D. Gardner and E. Chain (Proactinomycin. A "bacteriostatic" produced by a species of *proactinomyces*. *Brit. Jour. Exp. Path.* 1942). The name *proactinomycin* used to designate the active substance bears no chemical relation to *actinomycin*; it was derived from the generic name of the organism producing this substance. The term *bacteriostatic* used in this article is equivalent to *antibiotic* previously suggested by one of us (18) to designate the various bacteriostatic and bactericidal substances produced by microorganisms.

Very little of the active substance was extracted with ether at pH 3.0 to 8.5. The substance is precipitated from the aqueous extract, with some loss, by the addition of $(NH_4)_2SO_4$ up to 0.5 to 0.75 saturation. Alcohol and acetone are injurious to the active substance. It is partly retained on a Seitz filter. It is

TABLE 5

Bacteriostatic action of aqueous extracts of cultures of Micromonospora *sp.*

INCUBATION	SMALLEST AMOUNT OF EXTRACT, IN 10 ML. NUTRIENT-AGAR, INHIBITING GROWTH		
	B. subtilis	*S. lutea*	*S. aureus*
days	*ml.*	*ml.*	*ml.*
2	0.3	0.3	1.0
4	0.01	0.03	0.3
8	0.01	0.01	0.3
12	0.03	0.01	0.3
25	0.1	0.1	1.0
45	0.3	0.3	1.0

TABLE 6

Bacteriostatic action of water-extracts of 6-day-old cultures of Micromonospora *sp. on various bacteria*

TEST ORGANISM	SMALLEST AMOUNT OF EXTRACT, IN 10 ML., INHIBITING GROWTH
Aerobacter aerogenes	>1.0
Escherichia coli	>1.0
Pasteurella pseudo-tuberculosis	>1.0
Salmonella cholerae-suis	>1.0
Salmonella enteritidis	>1.0
Staphylococcus albus	0.3
Staphylococcus aureus	0.3
Staphylococcus muscae	1.0
Micrococcus lysodeikticus	0.1
Sarcina lutea	0.01
Bacillus brevis	0.03
Bacillus cereus	>1.0
Bacillus macerans	0.01
Bacillus megatherium	0.03
Bacillus mesentericus	0.03
Bacillus mycoides	>1.0
Bacillus polymyxa	0.03
Bacillus simplex	0.03
Bacillus subtilis	0.01

rapidly adsorbed by Norit at pH 7.8; attempts at elution by a series of citric-acid –disodium-phosphate buffers, ranging in pH from 3.0 to 7.0, were unsuccessful, negative results were also obtained with various extracting agents such as ammonia, ethanol, acetone, and amyl alcohol. The active agent is relatively thermostable.

Because of the fact that the biological action of *Micromonospora* was not essentially different from that of other antagonists, in that it had no activity against bacteria known to be resistant to other antibiotic agents, and because of the difficulties encountered in the preparation of cultures of this organism on a large scale, no further attempt was made to obtain concentrated and purified active material from it. The antibiotic substance is tentatively designated as *micromonosporin*.

Actinomyces sp., strain 47. This culture was isolated from a poor but limed soil diluted 1:50,000. It showed the following cultural and morphological characteristics:

Potato plug: Cherry-red, folded surface growth, turning brown; dark zone turning dark-green.

Gelatin: Brownish growth. Thin white aerial mycelium. Medium liquefaction. Black soluble pigment.

Litmus milk: Cream-colored growth; gray aerial mycelium; slow digestion of the milk.

Nutrient agar: Thin, slightly raised growth. No aerial mycelium. No soluble pigment.

Czapek's agar: Good growth; mouse-gray aerial mycelium. Brown-green to almost blue soluble pigment.

Morphology: Branching aerial mycelium, no spirals.

Activity: This culture possessed antagonistic properties against *E. coli* and various gram-positive bacteria. The antibiotic substance was water-soluble and ether-insoluble, and could, therefore, be classified with the streptothricin type.

Actinomyces sp., strain 78. This culture was isolated from a well-manured and limed soil, diluted 1:50,000. Its properties may be summarized briefly as follows:

Potato plug: Folded, barnacle-like growth, brownish. Scant white aerial mycelium. Black zone around growth.

Gelatin: Green growth, with thin white aerial mycelium. Green to black soluble pigment. Rapid liquefaction.

Litmus milk: Surface pellicle; white aerial mycelium. Rapid digestion of milk, black pigment.

Nutrient agar: Thin growth; thin white aerial mycelium. Faint brown pigment.

Czapek's agar: Thin growth, thin white-gray aerial mycelium.

Morphology: Loosely twisted spirals.

Activity: This culture was active against many gram-positive, as well as gram-negative bacteria, including *E. coli*. The antibiotic substance was soluble in ether, and may, therefore, be considered of the actinomycin type.

Actinomyces sp., strain 89. This culture was isolated from the same soil as strain 78.

Potato plug: Barnacle-like, gray growth. Thin, cream-colored aerial mycelium. Brown to black zone.

Gelatin: Good gray growth. White aerial mycelium. Moderate liquefaction. Brownish soluble pigment.

Litmus milk: Brown-colored growth. White aerial mycelium, with greenish tinge. Gradual digestion of milk.

Nutrient agar: Thin, brownish growth. No aerial mycelium; no soluble pigment.

Czapek's agar: Thin surface growth. Rose-lavender aerial mycelium. No soluble pigment.

Morphology: Closed, fist-like spirals.

Activity: This culture was highly active against both gram-positive and gram-negative bacteria. The antibiotic substance was water-soluble and ether-insoluble, and belongs, therefore, to the streptothricin type.

Actinomyces sp., strain 116. This culture was isolated from same soil as strain 47.

Potato plug: Grayish, folded growth. Abundant chalky white aerial mycelium. Color of plug, green to brown.

Gelatin: Brownish growth; gray aerial mycelium. Green-brown pigment. Slow liquefaction.

Litmus milk: Brown growth. White aerial mycelium. Slow digestion of milk.

Nutrient agar: Thin growth; thin white aerial mycelium. No soluble pigment.

Czapek's agar: Heavy growth; abundant gray aerial mycelium. Soluble brown pigment.

Morphology: Branching aerial mycelium, no spirals.

Activity: The activity of this organism was similar to that of strain 47.

Actinomyces sp., strain 138. This culture was isolated from the same soil as strain 47, in a dilution of 1:200,000.

Potato plug: Wrinkled, barnacle-like growth. Light-rose color. Abundant chalky white aerial mycelium. No soluble pigment.

Gelatin: Cream-colored growth. Abundant white aerial mycelium. No soluble pigment.

Litmus milk: Good surface growth. White aerial mycelium. Limited digestion of milk.

Nutrient agar: Thin growth; white aerial mycelium; no soluble pigment.

Czapek's agar: Thin growth. Rose-gray aerial mycelium. No soluble pigment.

Morphology: The type of sporulation characteristic of the *A. reticuli* group (14).

Activity: The antibiotic substance produced by this organism was active against gram-positive bacteria. It was ether-insoluble and water-soluble.

A summary of the cultural and antibiotic properties of the most important antagonistic actinomycetes so far known is presented in table 7. The group of microorganisms comprising the actinomycetes are thus shown to include a

TABLE 7

Characteristic properties of antibiotic substances produced by actinomycetes as compared with lysozyme

PREPARATION	LYSOZYME	ACTINOMYCETIN	ACTINOMYCES LYSOZYME*	STREPTOTHRICIN	ACTINOMYCIN	PROACTINOMYCIN	MICROMONOSPORIN
Source	Egg white	A. albus	A. violaceus	A. lavendulae	A. antibioticus	P. gardneri	Micromonospora sp.
Pigment production by culture		None	Black	Black in presence of oxygen	Black	Brown to black	Yellowish-pink, no exo-pigment
Chemical nature of active substance	Protein	Protein†	Protein, easily adsorbed. precipitated by ammonium sulfate and sodium chloride	Organic base	Polycyclic nitrogen compound		Unknown
Solubility	Water, not in alcohol, ether, or chloroform	Water, not in alcohol, ether, or chloroform	Water, not in alcohol, ether, or chloroform	Water, alcohol, not in ether or chloroform	Ether, alcohol, benzol, slightly in water	Ether and other solvents	Water, not in ether, alcohol, acetone
Action	Enzymatic	Enzymatic	Lytic	Primarily bacteriostatic	Primarily bacteriostatic and fungistatic	Bacteriostatic	Bacteriostatic
Bacterial constituent acted upon	Certain polysaccharides	Denatured protein	Unknown	Unknown	Unknown	Unknown	Unknown
Bacteria acted upon	Gram-positive, non-pathogenic cocci, little action on heat-killed bacteria	Acts mostly on dead bacteria†, gram-negative being more sensitive	Acts upon living and dead bacteria	Selective action upon certain gram-positive and gram-negative bacteria	Acts upon all organisms so far tested, more upon gram-positive than gram-negative bacteria	Gram-positive bacteria	Gram-positive species, especially aerobic, spore-bearing bacilli
Heat-resistance	Relatively thermostable at 70°C.; more resistant at low pH values	Thermolabile† (60°C.)	Thermostable, withstands boiling for 10–30 minutes	Thermostable	Thermostable	Thermostable	Relatively thermostable
Acid-resistance	Not sensitive	Lytic action reduced or completely destroyed by acid	Acts best at pH 7.1–7.8	Soluble in dilute acid, destroyed by concentrated acid	Resistant to acids, sensitive to alkalies	Sensitive to acid, soluble in alkali solutions	Destroyed by concentrated acids
Special properties	Some bacteria (Sarcina and M. lysodeikticus) highly sensitive	Streptococci, staphylococci and B. meg atherium most sensitive	Acts selectively on bacteria. Produced on synthetic and not on organic media	Has been concentrated and purified	Red pigment. Has been crystallized. Highly toxic to animals	Precipitated from aqueous solution by base precipitants	Precipitated by (NH₄)₂SO₄, destroyed by alcohol or acetone. Readily adsorbed on Norit.

* Proof of identity with lysozyme is open to question.

† Lipoid substance accompanies protein as a bactericidal agent, the protein being a lytic agent, the lipoid being thermostable and killing only gram-positive bacteria.

number of antagonists varying greatly in the nature of antibiotic action, in the chemical nature of the active agent, and in the specific organisms affected.

SUMMARY

Actinomycetes possessing antagonistic properties against bacteria and fungi are widely distributed in nature, especially in soils and in composts.

Two hundred and forty-four cultures were isolated at random from different soils; of these, 106 cultures or 43.4 per cent possessed some antagonistic properties, and 49 cultures or 20 per cent were highly antagonistic. Similar relations were observed by examining a large series of well-identified organisms kept for a number of years in a type culture collection.

Although antagonistic forms were also found among the genera *Proactinomyces* and *Micromonospora*, they were most abundantly represented by members of the genus *Actinomyces*.

Some of the most active antagonistic cultures were studied in detail, and several antibiotic substances were isolated.

These antibiotic substances vary greatly in their chemical composition and in their mode of action. They are highly selective in nature, affecting different organisms in a different manner. They are not only bacteriostatic, but also bactericidal. Some are highly bacteriolytic, a property widely distributed among certain types of actinomycetes.

A brief description of the most active antagonists, isolated from soils and from other substrates, is presented.

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INFLUENCE OF THE CHEMICAL COMPOSITION OF ORGANIC MATTER ON THE DEVELOPMENT OF MOLD FLORA IN SOIL[1]

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A number of investigators have found that the mold flora of the soil is markedly influenced by the type of organic matter present. Jensen (1), for example, has found that the fungus flora varies with the environment. *Mucor* species were found in larger numbers in cultivated soils than in marsh, moor, and forest soils, whereas *Zygorynchus* and *Absidia* were found to predominate in forest and moor soils.

Waksman (4, pp. 238–239) concluded that differences in the composition of organic matter give rise to variations in the kind of soil fungi developing. Stable manures stimulated the development of *Penicillium* and members of the *Mucoracae*. Pure cellulose plus available nitrogen brought about the development of species of *Trichoderma*, *Fusarium*, *Verticillium*, and *Penicillium*.

Martin (2) found that *Mucor*, *Rhizopus*, and *Alternaria* predominate in soils treated with alfalfa roots. *Cladosporium* was the major form in straw-treated soils, and *Aspergillus* and *Penicillium* were dominant in sweet-clover–treated soils.

The process of decomposition has been shown to result in a progressive change in the constituents available to microorganisms (2, 3). The fact is apparent that this change in constituents may be reflected in turn by a variation in the kinds of molds which predominate at any given stage in the decomposition process. With this in mind, the following experiment was conducted. The specific purposes of the experiment were: first, to determine the changes in the proportions of the various constituents of organic matter during the decomposition process; second, to study the types of molds that develop during decomposition; and third, to determine whether any parallelism exists between the types of organic constituents that predominate at any stage of decomposition and the kinds of mold that will be dominant in the soil flora.

EXPERIMENTAL MATERIALS AND METHODS

The soil used in this experiment was a dark gray, sandy loam of local origin, the series of which has not yet been established. It was air-dried and passed through a 2-mm. sieve, after which 250-gm. portions were weighed into a series of half-pint bottles. Sweet clover in the half-grown stage was collected, dried, ground, and passed through a 2-mm. sieve. This was incorporated in 4 per cent amounts in the bottles of soil. Sufficient water was added to the mixtures to bring the moisture content up to 55 per cent water-holding capacity. Similar preparations were set up with the following types of organic matter: alfalfa (*Medicago*

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sativa), whitetop (*Lepidium draba*), Russian thistle (*Salsola pestifer*), wheat straw, and corn fodder. The samples were then incubated at 28° C.

At each 10-day interval over a period of 140 days, a bottle from each set was sampled, and mold counts were made. The method of sampling consisted of removing, aseptically, the top half inch of the soil in the bottles and then taking, to a depth of 2 inches, duplicate 5-gm. samples. After making dilutions in sterile water, plates were poured in duplicate using a synthetic medium made according to Waksman's formula (4, p. 19). Plates were incubated for 4 days at 28° C. Numbers and kind of molds were then determined.

In order to follow the chemical changes in these different organic materials as decomposition progressed, 1200-gm. portions of each of the six organic materials were placed separately in one-half gallon jars. Sufficient filtrate from a soil suspension was added to the organic matter in each jar to bring the moisture content up to 55 per cent of saturation capacity. This material was incubated at 28° C. for 120 days. At 20-day intervals, 5-gm. samples were withdrawn, dried, and analyzed, by Waksman's method (5), for percentage of sugar, starches, hemicelluloses, celluloses, and lignins.

Because of the inherent difficulty of making direct determinations of the constituents of the organic matter mixed with soil, it was necessary to study the chemical changes in the manure decomposition in containers with organic matter alone. The mold development studies were carried on with organic matter and soil mixed. In adopting this procedure, it was assumed that, since the same moisture content had been used with the organic matter and with the organic matter and soil mixed, and the type of organism present was essentially the same in both cases, the decomposition change would be more or less parallel. It is recognized that this assumption may not be wholly valid, but the difficulties involved made this the most logical method of approach.

RESULTS AND DISCUSSION

The chemical composition of sweet clover at the beginning of the decomposition period and at 20-day intervals is given in figure 1a. The initial analyses show a relatively high water-soluble sugar and starch content, and a low lignin content. As decomposition proceeded, the chemical composition changed. The sugars originally present were virtually exhausted in the first 20-day period. Throughout the remainder of the study, the sugars which resulted from hydrolysis of the higher carbohydrates disappeared as quickly as they were produced. This is evidenced by the low percentages at each subsequent analysis. The results with soluble starches were similar to those with the sugar.

With the removal of sugars and much of the starch in the first 20 days, the hemicellulose and cellulose fractions begin to assume more prominence. Both increase up to the first 20 days, after which the cellulose curve begins to decline, at first rapidly but after 60 days very slowly. The hemicellulose curve, on the other hand, does not decline simultaneously with that of cellulose, but rises to a peak between 40 and 60 days. This would seem to indicate that the cellulose decomposed more rapidly than did the hemicellulose.
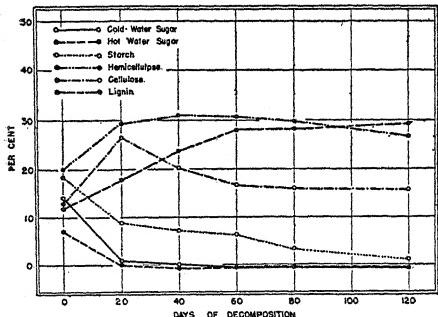
FIG. 1a. CHEMICAL COMPOSITION OF SWEET CLOVER TOPS AT 20-DAY INTERVALS OF DECOMPOSITION

FIG. 2a. CHEMICAL COMPOSITION WHITETOP AT 20-DAY INTERVALS OF DECOMPOSITION
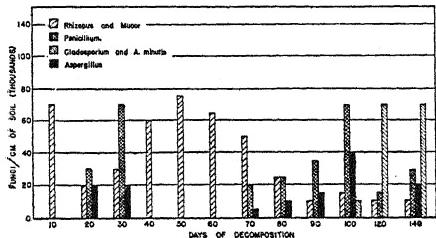
FIG. 1b. NUMBERS AND KINDS OF FUNGI DEVELOPED DURING THE DECOMPOSITION OF SWEET CLOVER TOPS IN SOIL

FIG. 2b. NUMBERS AND KINDS OF FUNGI DEVELOPED DURING THE DECOMPOSITION OF WHITETOP IN SOIL
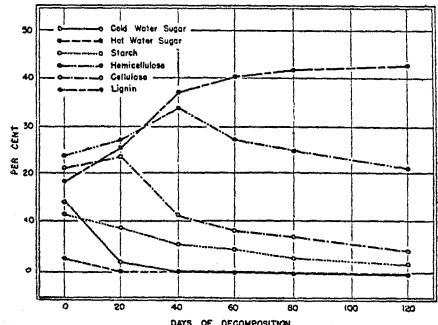
FIG. 3a. CHEMICAL COMPOSITION OF CORN LEAVES AT 20-DAY INTERVALS OF DECOMPOSITION
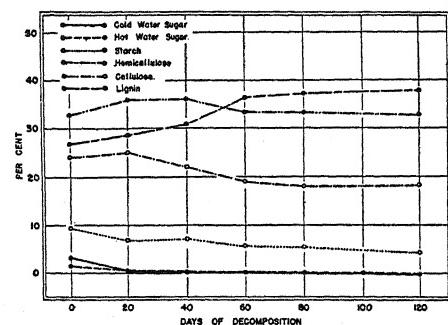
FIG. 4a. CHEMICAL COMPOSITION OF STRAW AT 20-DAY INTERVALS OF DECOMPOSITION
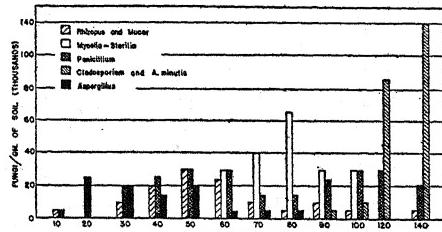
FIG. 3b. NUMBERS AND KINDS OF FUNGI DEVELOPED DURING THE DECOMPOSITION OF

FIG. 4b. NUMBERS AND KINDS OF FUNGI DEVELOPED DURING THE

Lignin is rather resistant to decomposition. There was a rapid increase in percentage up to the 60-day period; then, for the rest of the study, there was a continuous, slow increase as the slightly less resistant materials were decomposed.

Figure 1b shows the influence of the chemical changes on the mold flora of the soil. An examination of this graph shows the mold groups Rhizopus nigricans, Mucor rouxi, Penicillium glaucum, Aspergillus niger, and the dark-colored Cladosporium, Alternaria, and Aspergillus minutis to have appeared in separate and distinct cycles throughout the course of decomposition. The time when each of the mold groups is in predominance correlates with a distinct phase in the chemical breakdown of the sweet clover material in figure 1a.

In the soil treated with sweet clover tops, the Rhizopus and Mucor began development at the 10-day point, decreased during the 20- and 30-day periods, then increased rapidly up to a maximum at 50 days. By 60 days the cycle had begun to decline, and after 80 days these molds grew very feebly.

This period of Rhizopus-Mucor predominance virtually coincided with the period of most rapid decomposition of the celluloses and hemicelluloses. This would indicate that these molds are associated with the period in which rapid decomposition of the more easily available carbohydrates occurred. Inasmuch as sugars seem to stimulate the growth of Rhizopus and Mucor, it is not unreasonable to assume that these molds have been stimulated by sugars produced during the rapid hydrolysis of hemicelluloses and celluloses. In addition, it will be noted that the species of Rhizopus were very prominent at the 10-day point, but had declined sharply in 20 days. It was during these 20 days (see fig. 1a) that the sugars originally added with the organic matter were completely dissipated. That these molds are favored by high sugar availability is thus suggested.

With the decline of Rhizopus and Mucor, the Penicillium sp. and Aspergillus niger become prominent at the 70-day period. They increase rapidly in relative activity from that point up to 100 days of decomposition, when they appear to reach their peak. They decline sharply at 120 days then increase again at the 140-day period. The apparent discrepancy at this 140-day point cannot be explained on the basis of information now available.

The appearance of these molds at a time when the celluloses and hemicelluloses have reached a fairly stable state seems to indicate that these fungi derived their energy from these organic compounds, which are less readily available than sugar or starch.

Beginning at the 100-day period, the dark-colored molds, chiefly Cladosporium, Alternaria, and Aspergillus minutis developed. They increased rapidly and became very dominant during the 120–140-day period, when the cellulose curve was practically stabilized and the resistant lignins were the dominant constituents of the sweet clover.

Figures 2a and 2b record the results obtained with whitetop. The initial composition of this material differed markedly from that of the sweet clover tops in that the whitetop was very much lower in sugar content, somewhat lower in starches, and very much higher in lignin.

Few *Rhizopus* and *Mucor* molds developed during the first 10 days. As decomposition proceeded and sugars were made available from the higher carbohydrates, as evidenced by the drop in percentage of celluloses and hemicelluloses, the *Rhizopus* and *Mucor* molds followed through their cycle, completing it within 80 days. The peak of the cycle occurred at the 30–40-day period, which corresponds well with that part of the chemical composition curve showing the most rapid decomposition of the cellulose and hemicellulose contents, as was the case with sweet clover.

During this 40-day interval, *Penicillium* and *Aspergillus* species were present, but it was not until after the 60-day period that they became dominant. At this time, the cellulose and hemicellulose curves were being stabilized. During the 70–100-day period, the *Penicillium* species were present in very large numbers and the *Aspergillus*, to a somewhat lesser extent.

After 90 days, which followed a period when the cellulose and hemicelluloses had reached equilibrium, the sugars were completely lacking and the lignin content was still slowly rising. The dark molds appeared at this time and increased rapidly, becoming very noticeable after 140 days.

It is noted in figure 3*b* that the *Rhizopus-Mucor* group of molds were unusually dominant in the soil treated with corn fodder. Large numbers of these fungi appeared in the first plates poured and remained as the dominant mold throughout the first 120 days of organic matter decomposition. Figure 3*a* shows a very rapid decomposition of the carbohydrates over the whole range of 120 days. Unlike the other organic materials, no static stages in the cellulose and hemicellulose contents were reached. The effects of such a decomposition on the mold flora are readily seen from figure 3*b*. The *Penicillium* and *Aspergillus* species made a feeble appearance at 90 days, but did not exceed the *Rhizopus-Mucor* group until the 140th day. Had the experiment been continued for another 60 days, it is quite probable that the *Penicillium* group and the dark-colored mold group would have behaved as they did in the sweet clover and whitetop studies.

An examination of the mold species present in straw-treated soil (fig. 4*b*) shows *Aspergillus* species to be present throughout the whole 140-day period. After the first 20 days, the *Penicillium* species also were in evidence. Beginning at 90 days, the dark molds increased rapidly until, at 140 days, there were 140 per milligram of soil. It will be noted from figure 4*a* that the changes occurring in the carbohydrates at this period are very slight. It is interesting to note, too, that the *Rhizopus-Mucor* reach their maximums at the 50-day period, which corresponds exactly with the period of most rapid decomposition as interpreted by the slope of the lignin curve.

The chemical composition and mold count data for Russian thistle and alfalfa tops indicate the same phenomenon as that in the previous illustrations, that available sugars favor the development of *Rhizopus* and *Mucor*. Later stages of cellulose and hemicellulose decomposition are conducive to *Penicillium* and *Aspergillus* growth, and during the latest stage of decomposition, when lignins are prominent, dark-colored, dense mycelial fungi such as *Cladosporium*, *Alternaria*, and *Aspergillis minutis* assume prominence.

CONCLUSIONS

Changes in the chemical composition of organic materials as they undergo decomposition in the soil seem to effect a change in the mold flora.

The higher the percentage of readily decomposable carbohydrate materials, i.e., sugars, starches, and some hemicellulose and cellulosic materials, the greater the predominance of species of *Mucor* and *Rhizopus* in proportion to other molds present in the soil–organic-matter mixture.

When a stable hemicellulose and cellulose fraction has been produced in the soil, little of the more easily decomposed carbohydrate material remaining, molds which presumably prefer this material, i.e., *Penicillium glaucum* and *Aspergillus niger*, predominate.

When lignin is the chief constituent remaining of the original plant material, species of *Cladosporium*, *Alternaria*, and *Aspergillus minutis* are found in greatest number.

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SOME FUNGAL INFECTIONS OF CITRUS IN RELATION TO NUTRITION[1]

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The occurrence and severity of many parasitic plant diseases are known to be markedly affected by soil conditions and by deficiencies, excesses, and balance of mineral nutrients. A partial review of this field, with special reference to the control of root diseases, has been given by Garrett (8). Recent studies dealing with one or more phases of this problem have been reported by Henderson (9), Leach and Davey (12), Young and Tharp (21), Eaton (6), Smith and Walker (17), Kent (10), Wager, (20), Bain and Chapman (2), Pryor (14), Spencer (18), Russell and Sallans (15), Adams *et al.* (1), and Tisdale and Dick (19). Fertilizers and soil conditions may influence disease through effects on the numbers of the pathogen in the soil (e.g., chemical and biological conditions favoring or depressing growth of the organisms), effects on the pathogenicity of the organism, and effects on the resistance of plants to invasion (e.g., morphological and biochemical changes). These may operate singly or in combination.

In connection with our studies of citrus in sand and solution cultures, a number of interesting cases of parasitic diseases brought on by nutritional conditions have come to the writers' attention. Because of the current interest in this general problem, as well as the practical implications in relation to certain obscure disorders of citrus in the field, two of these cases are described in some detail.

EXPERIMENTAL

The observations reported herein were made on young citrus trees growing in solution cultures out of doors. One of the experiments was set up to study the effect of various potassium levels on tree growth, chemical composition, and fruit quality, and the other was a phosphate experiment with a similar object in view.

Potassium experiment

In the potassium experiment a group of 4-year-old orange trees (Valencia and navels on sour rootstock) were transferred in June, 1940, from sand cultures of 100-liter capacity to solution cultures of 700-liter capacity. These containers (cylindrical cement conduits) were provided with cement bottoms, painted inside and out with an asphaltum product, and three-quarters buried in the ground. Painted cement lids split into semicircles, with a semicircular hole at the center of each, to accommodate the tree, were used as covers (see figures 1 and 2).

The 20 trees of this experiment were divided into three groups, each group being given a complete nutrient solution containing potassium at a different level. The composition of the nutrient solutions and certain other details of the experi-
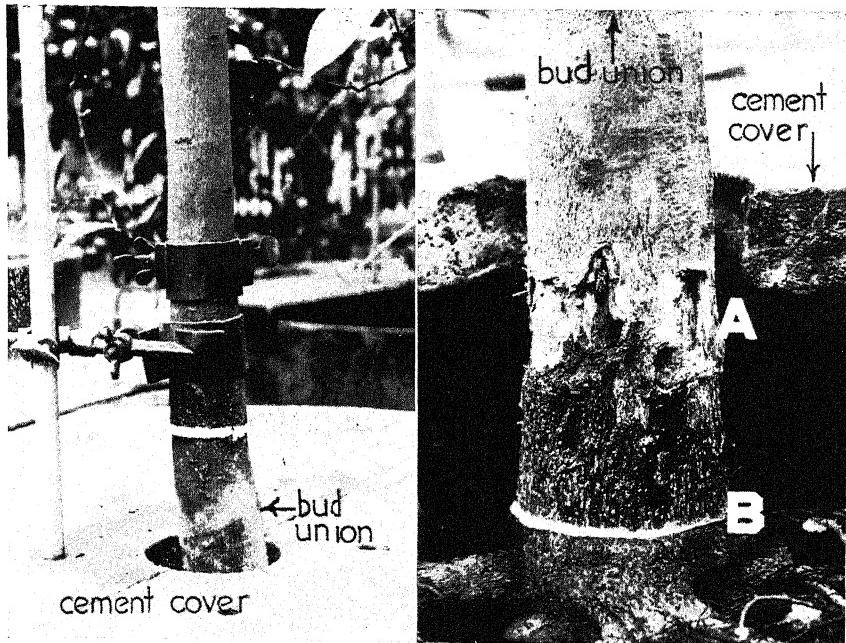
FIG. 1. TRUNK SECTIONS OF TREE 24, SHOWING GUMMOSIS LESIONS DUE TO PHYTOPHTHORA PARASITICA IN RELATION TO SOLUTION-CULTURE LEVEL, CIRCULAR HOLE IN CEMENT COVER, AND BUD UNION

A, Brown rot gummosis lesions on sour orange root; B, solution-culture level
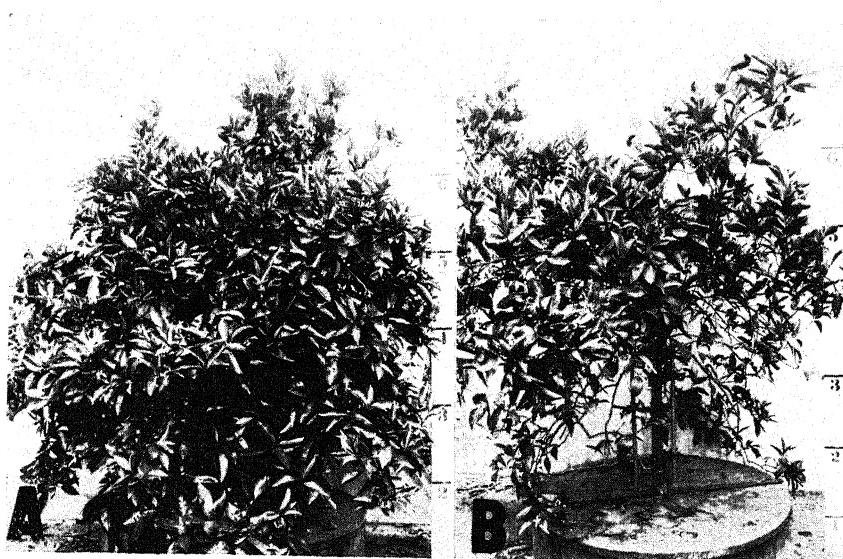
FIG. 2. REPRESENTATIVE TREES GROWING IN LOW- AND HIGH-POTASSIUM SOLUTIONS AS THEY APPEARED IN APRIL, 1942

A, Tree 22 in low-potassium–high-calcium solution; B, tree 24 in high-potassium–low-calcium solution, attacked by *Phytophthora* fungus. Poor tree condition preceded the appearance of gummosis lesions.

ment are set forth in table 1. The low-potassium solutions were made up to contain sufficient amounts of all nutrients, except potassium; the medium-potassium group to contain sufficient, but not excessive amounts of potassium; the third, to contain excessive amounts of potassium. In order to keep anion levels essentially constant, calcium was decreased in the high-potassium cultures. This decrease in calcium also served to accentuate the excess of potassium through the operation of the calcium:potassium antagonism (4).

The solutions were continuously aerated, and the reaction was maintained at approximately pH 5.0, adjustments being made with H_2SO_4 or NaOH as re-

TABLE 1

Composition of nutrient solutions used in potassium experiment with navel and Valencia orange trees*

TREATMENT	TREE NUMBERS	VARIETY	MILLIEQUIVALENTS PER LITER†								P.P.M.‡		
			Ca	Mg	K	Na	Cl	PO$_4$	SO$_4$	NO$_3$	B	Mn	Al
Low potassium	4, 15, 19, 22 6, 13, 14, 18, 25§	Navel Valencia	12.11	5.50	0.20	1.37	0.57	0.30	8.51	10.00	0.5	0.5	1.0
Medium potassium	16,‖ 17 2, 8, 23§	Navel Valencia	12.11	5.50	1.05	1.27	0.57	0.30	9.26	10.00	0.5	0.5	1.0
High potassium	3, 24 1‖, 7, 21§, 26§	Navel Valencia	3.14	5.50	10.02	1.27	0.57	0.30	9.26	10.00	0.5	0.5	1.0

* All these trees were purchased as 1-year-old budded trees on sour stock from the Armstrong Nurseries, Ontario, California, in June, 1936. They were grown for 4 years in sand cultures supplied with several different levels of nitrate.

† The sums of cations and anions listed do not balance, since NaH_2PO_4 was used as a source of phosphorus.

‡ Ferrous sulfate was added at the rate of 0.1 p.p.m. Fe thrice weekly.

§ Trees 21, 23, 25, and 26 are of the same age and were handled similarly to the others except that they had been included in another solution-culture experiment up to March, 1941. They had not, therefore, been grown in nutrient solutions of the composition indicated in this table prior to the aforementioned date.

‖ Trees 1 and 16 were discarded in August, 1940, because of root rot, and 1-year-old budded navel orange trees on sour rootstock were substituted in their places.

quired. Phosphate, potassium, and nitrate were determined, and adjustments were made with sufficient frequency to keep the concentration of each reasonably constant. Water taken out by the tree was compensated by additions of distilled water as needed. The solutions were renewed at monthly intervals.

The roots of all of these trees were in a healthy condition when removed from the sand, which was washed out with a forceful spray of tap water, but they were densely matted, especially toward the surface. Within several weeks after transfer to the solution cultures, more or less root rot (gelatinization of fine roots) developed, especially in the thickly matted parts of the root systems. In the belief that the aeration rate and consequent movement of the solution were not

sufficiently vigorous to maintain an adequate oxygen concentration in the solution in contact with the interior of the root mat, the aeration rate was increased and the severely rotted sections were pruned away. Following this treatment, all of the trees, save 1 and 16, recovered. The root rot on these two trees had become so severe that they were finally discarded, and two 1-year-old budded navel orange trees on sour rootstock were substituted in their places on August 29, 1940. The nature of the organism responsible for this rot was not determined.

No effects of the various potassium levels became apparent until the fruit began to reach full size and to mature in the winter of 1940-41. At this time, the fruit on both the Valencia and the navel trees in the high-potassium–low-calcium cultures began to display a number of abnormalities. The Valencias did not color so rapidly or so completely as those of cultures at lower potassium levels, and the rind texture was extremely coarse. The navel fruits were large, many were puffy and misshapen, and when they were picked and graded many showed soft spots on the rinds, suggestive of the early stages of water spot (11); and a number of fruits showed black rot, the disease caused by *Alternaria citri*. None of the fruits produced on the medium- and low-potassium cultures showed these abnormalities.

During the spring of 1941 the high-potassium–low-calcium trees began to lose more leaves than the trees in the other solutions, though there were no discernible symptoms of injury on the leaves, stems, or trunks, except that the spring-cycle leaves in all the high-potassium cultures displayed manganese-deficiency patterns; these cleared up, however, as the season progressed. Leaf and fruit analyses showed a subnormal calcium content and high potassium levels.

In the course of the summer, the typical gumming which characterizes brown rot gummosis (7) was noted on the sour stock part of tree 21 (high-potassium–low-calcium series). Subsequently, trees 3 and 24 of this same series showed similar symptoms. Tree 1, in this same group, developed severe root rot and finally died. The lesions on the trunks of trees 3, 21, and 24 were cut away in accordance with directions given by Klotz and Fawcett (11), and callusing took place along the cut margins of the bark of trees 3 and 24. Tree 21, however, did not recover and was finally discarded. Hence, of the six trees in this treatment, three became affected with brown rot gummosis, and another developed a root rot so severe that it had to be discarded. None of the trees in any of the lower potassium cultures showed these troubles. Though the gummosis appeared to be temporarily arrested by cutting away the diseased tissue, tree 24 is now (June, 1942) showing fresh gumming.

A study of the roots in a number of the cultures, including those showing brown rot gummosis, was made by L. J. Klotz, of this station. He was able to isolate *Phytophthora parasitica* from nearly all. It seems certain, therefore, that this organism was present in all of the cultures, but up to the present only the high-potassium-low-calcium trees have shown symptoms of this disease.

Trees 7 and 26 of the high-potassium–low-calcium group, though showing marked indications of malnutrition (sparse foliage and some dieback), are up to

the present not affected with gummosis. Thus, the fungal infection was in all probability brought on by the lowering of the usual resistance of the sour stock due to an unfavorable potassium:calcium ratio. The trees of this group have shown some of the symptoms that characterize calcium deficiency; however, calcium deficiency symptoms vary, depending on whether produced under conditions of high or of low potassium. Hence, it cannot be assumed that poor tree condition is due to low calcium as such, or to high potassium alone. The authors believe that it is the combined effect of both conditions which is responsible for the malnutrition.

It is of interest that this disease developed on trees budded on sour stock, the bark and roots of which are ordinarily very resistant to various *Phytophthora* spp. Conditions for invasion, however, were ideal in this experiment. The position of the gummosis lesions in relation to the bud union, the opening in the cement lids, and the water level in the solution culture are shown in figure 1. Though the bud union on all the trees was definitely above the top of the cement cover and therefore dry at all times, the part of the sour orange trunk passing through the hole in the cement covers and into the solution below was continuously moist. It is well recognized that such conditions are conducive to invasion by the brown rot organism. Despite these favoring conditions, the trees growing in nutrient solutions suitable for healthy growth have shown no symptoms of disease up to the present time.

The unhealthy growth characteristics of tree 24 in high-potassium–low-calcium cultures compared with the healthy growth of a representative tree (No. 22) in the low-potassium–high-calcium cultures is illustrated in figure 2.

Phosphorus experiment

In June, 1940, 21 navel orange trees on sour rootstock, 1 year old from the bud, were transplanted from the nursery bare root into complete solution cultures of various phosphate levels. The containers were 273-liter vitrified tile provided with cement bottoms. They were in a screened enclosure out of doors and were about four-fifths buried in the ground. The composition of the nutrient solutions is shown in table 2. These cultures contained sufficient of all nutrients for good citrus growth, except that the low-phosphate series were intended to be slightly deficient in this element.

The solutions were continuously aerated as in the potassium experiment; the reaction was maintained at approximately pH 5.0, and the concentration of phosphate and other constituents was kept essentially constant by frequent determination, adjustment, and periodic renewal.

The plants in all cultures grew well and made considerable top and root growth during the first few months By October, 1940, a slight difference was noted in root growth, the high- and medium-phosphate plants showing some tendency toward root stubbiness, and on a number of these roots a black fungus, later identified by Klotz as *Thielavia basicola*, had become established. By March, 1941, the tendency to root stubbiness and the fungal infection had become more pronounced in the high- and medium-phosphate cultures, and even the roots of

the low-phosphate cultures showed more fungal infection and stubbiness than previously.   During the summer and fall of 1941, however, the roots on the low-phosphate cultures became decidedly better than those of the medium- and high-phosphate cultures.   Although some fungus infection was still present on the roots of all the low-phosphate plants, it was much less abundant than on the roots of the trees in the other cultures.   This same condition persisted throughout the winter and spring of 1942, and at the present time continues unchanged.   So far as is known, *Thielavia basicola* has not previously been reported on citrus roots.

Inasmuch as Morgan and Anderson (13), Doran (5), and others found that the activity of this organism on tobacco roots was reduced under field conditions by increasing soil acidity, cultures 2 and 18 of the high-phosphate group were acidified.   The acidity was lowered from the prevailing pH 5.0 level to pH 3.5 on February 25, 1942.   No change was apparent from this treatment until abundant healthy new roots, free of the fungus, began to emerge in May.   It is too early to say whether this treatment will prove successful as a control measure,

TABLE 2

Composition of nutrient solutions used in phosphorus experiment with navel orange trees

TREATMENT	TREE NUMBERS*	MILLIEQUIVALENTS PER LITER†								P.P.M.‡		
		Ca	Mg	K	Na	Cl	PO₄	SO₄	NO₃	B	Mn	Al
Low PO₄	7, 8, 9, 12, 13, 14, 21, 22, 23	9.04	4.52	1.20	1.30	0.57	0.10	10.43	5.03	0.5	0.5	0.5
Medium PO₄	4, 5, 6, 15, 16, 24	9.04	4.52	1.20	1.77	0.57	1.50	10.43	5.03	0.5	0.5	0.5
High PO₄	1, 2, 3, 17, 18, 19	9.04	4.52	1.20	2.93	0.57	5.00	10.43	5.03	0.5	0.5	0.5

* Washington Navel orange trees on sour orange rootstock.

† The sums of cations and anions listed do not balance, since NaH_2PO_4 was used as a source of phosphorus.

‡ Ferrous sulfate was added at the rate of 0.1 p.p.m. Fe thrice weekly.

but it appears promising.   Microscopic examination of roots clearly shows fresh lesions and mycelial growth on the new roots of the trees in high-phosphate cultures maintained at pH 5.0, but no infection can be seen on the new roots of the trees in the pH 3.5 cultures.

In his soil acidification experiments to control tobacco root rot caused by *Thielavia basicola*, Doran (5) found that, whereas sulfuric acid, sulfur, and aluminum sulfate were effective, phosphoric acid, though lowering pH to the same degree, actually increased the disease.

The difference in growth of roots in a low-phosphate culture (tree 7) as compared with growth in a high-phosphate culture (tree 17) is shown in figure 3 *A* and *B*.   Sections of root systems from these plants showing the short laterals and dark-colored lesions on the roots of trees growing in the high-phosphate cultures as compared with the longer laterals of the less infected roots in the low-phosphate cultures are shown in figure 3 *C* and *D*.   The new healthy root growth is also shown emerging from one of the high-phosphate cultures where the reaction was lowered to pH 3.5 (fig. 3 *E*).

Top growth has been depressed somewhat by the fungal infection of these plants, as is shown in figure 4 (trees 7 and 17). No symptoms of malnutrition,
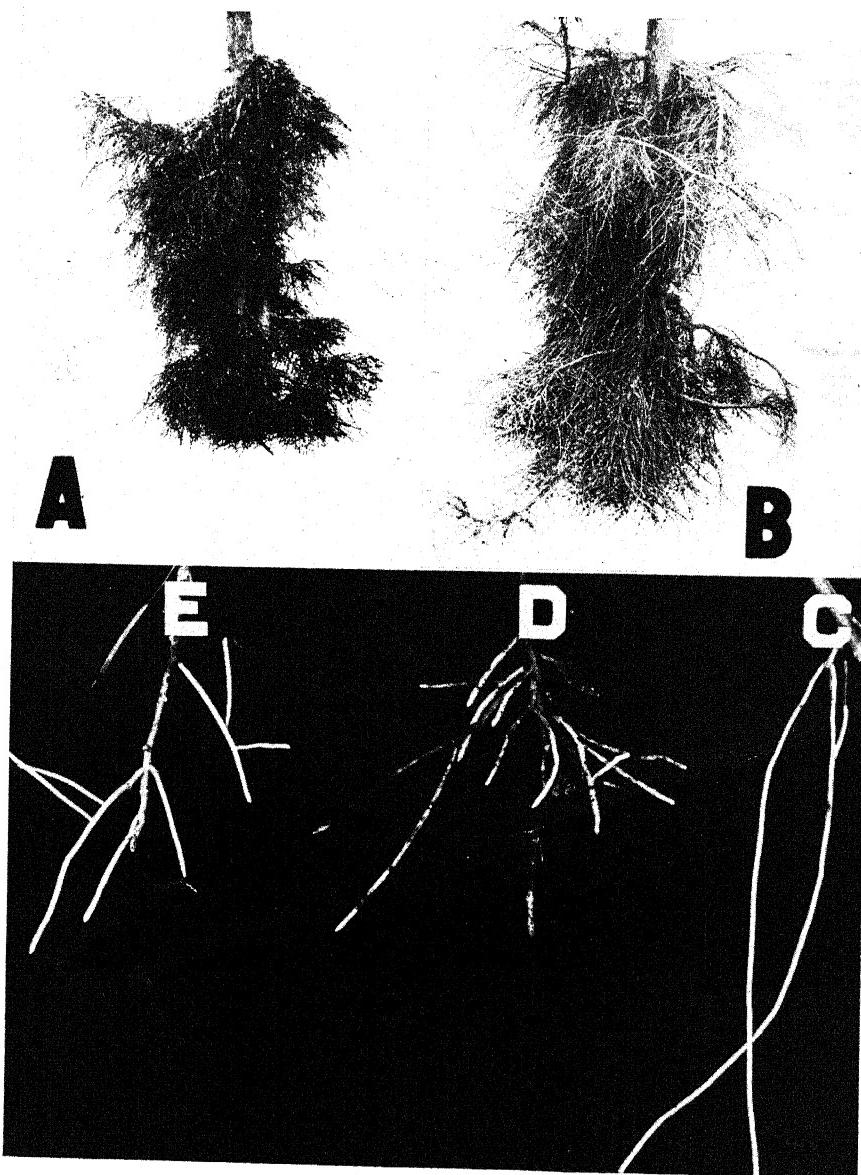
FIG. 3. A, ROOT SYSTEM OF TREE 17, SEVERELY INFECTED WITH THIELAVIA BASICOLA, IN HIGH-PHOSPHATE CULTURE; B, HEALTHY ROOT SYSTEM FROM LOW-PHOSPHATE CULTURE 7; C, NEW ROOTS OF LOW-PHOSPHATE CULTURES SHOWING LITTLE FUNGUS; D, SEVERE FUNGAL INFECTION ON NEW ROOTS OF HIGH-PHOSPHATE CULTURE; E, FUNGUS-FREE NEW ROOTS FROM HIGH-PHOSPHATE CULTURE REDUCED TO pH 3.5

however, are evident in the tops of the plants of the medium- and high-phosphate cultures, but the growth rate is not so rapid in these as in the low-phosphate cultures.

FIG. 4. COMPARATIVE TOP GROWTH OF NAVEL ORANGE TREES IN HIGH- AND LOW-PHOSPHATE NUTRIENT SOLUTIONS

A, Tree 17, with severe root infection of *Thielavia basicola*, growing in high-phosphate solution; B, tree 7, in low-phosphate culture, root infection slight. Aside from reduced growth, the top of the root-infected plant appears green and healthy. Photographed April, 1942.

DISCUSSION

Many other instances of root rot brought on by prolonged mineral deficiencies or excesses, drastic pruning, or sudden changes in the concentration of nutrient solution have been noted in the course of this work. The causal organisms in these cases were not identified.

Although no studies have yet been made of the specific morphological and biochemical relationships involved, these observations emphasize the delicate balance existing between host and parasite. It is evident that, although a citrus tree may appear entirely healthy above ground, its growth and yield are perhaps being impaired by the activity of organisms at work on the roots. Obviously, all degrees of injury are possible, depending upon the degree of favorableness or unfavorableness of the environment for the tree, on the one hand, and for pathogenic or semipathogenic organisms, on the other. That the increase or decline of citrus trees in some sections of California may be due to some such set of relationships is suggested by the foregoing observation. Of particular significance in this connection is the fact that considerable accumulations of phosphate (3) and potassium[2] have occurred in many commercial citrus orchards of California

[2] Unpublished data by S. M. Brown. On file at the University of California Citrus Experiment Station, Riverside, California.

as a result of past fertilization practices.   A survey is now under way to determine whether conditions with respect to phosphorus, potassium, and other elements comparable to the ones in these cultures exist anywhere in the California citrus-growing regions.

SUMMARY

In the course of solution-culture experiments with citrus a number of cases of disease resulting from nutritional unbalance have been noted.   Two of these are described in some detail.

Four-year-old navel and Valencia orange trees on sour orange rootstock growing out of doors in solution cultures of high-potassium–low-calcium content became infected with brown rot gummosis.   Under similar conditions of culture, but with more favorable potassium:calcium ratios, no symptoms of this disease developed, though it was possible to isolate *Phytophthora parasitica* from the roots of these apparently healthy trees.   The fruits on the navel orange trees nutritionally unbalanced by an unfavorable potassium:calcium ratio showed some water spot disease on the rinds, and a considerable number of fruits became infected with *Alternaria citri*.

In a somewhat similar outdoor solution-culture experiment with navel orange trees on sour root, the plant roots in cultures receiving medium- and high-phosphate levels (1.5 to 5.0 m.e. per liter) became seriously infected with *Thielavia basicola*.   The low-phosphate trees (slightly phosphorus-deficient), although showing some infection, were much less seriously affected.

The reaction of all of these cultures had been maintained close to pH 5.0.   Increasing the acidity to pH 3.5 in two of the high-phosphate cultures markedly checked growth of *Thielavia basicola*, and the new roots that developed subsequently showed no symptoms of reinfection.

These observations may have some practical significance in relation to citrus disorders in California, since phosphate and potassium have accumulated markedly in the soils of many old citrus orchards as a result of the continued use of manures and mixed fertilizers.

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BOOKS

Annual Review of Biochemistry. Vol. XI. Edited by JAMES MURRAY LUCK and JAMES H. C. SMITH. Annual Reviews, Inc., Stanford University, 1942. Pp. 736. Price, $5.

No matter what phase of biochemistry and its related fields one may be engaged in, he will find several articles in this volume which will be of great interest and value. For the soil chemist, the papers dealing with lignin, vitamins, mineral nutrition of plants, plant-tissue cultures, and microbiology are of special importance. Other papers are concerned with oxidations and reductions; x-ray studies of compounds of biochemical interest; hydrolytic enzymes; the chemistry of fats, oils, steroids, proteins, and amino acids; the metabolism of phosphorus, fats, carbohydrates, and proteins; and various phases of such diverse topics as hormones, nutrition, avian biochemistry, animal pigments, alkaloids, and immunochemistry. References are given to the work of some 4,000 scientists who are engaged in biochemcal research.

Diseases of British Grasses and Herbage Legumes. By KATHLEEN SAMPSON and J. H. WESTERN. Cambridge University Press. The Macmillan Company, New York, 1941. Pp. 85, figs. 15, plates, 8. Paperbound. Price, $1.50.

A report covering 20 years of study of fungus, virus, and other diseases affecting grasses and clovers at the Welsh Plant Breeding Station and at centers of seed production of the Aberystwyth strains of herbage plants. Special attention has been paid to the pedigree strains of these grasses and clovers. An attempt has been made to assess the relative economic importance of the different parasites.

Optical Methods of Chemical Analysis. By THOMAS R. P. GIBB, JR. McGraw-Hill Book Company, Inc., New York, 1940. Pp. 391, figs. 300. Price, $5.

A concise factual presentation of information on the construction and use of optical instruments employed in chemical procedures. The several chapters deal with spectrochemical analysis, the spectrophotometers, the colorimeter and related instruments, the microscope, the refractometer, and the polariscope, with two additional chapters on elementary crystallography and the use of the polarizing microscope in the identification of crystals. Almost every analytical chemical laboratory will find this book of value as a ready reference on instruments and methods that are being employed with increasing frequency.

Soil Science Society of America Proceedings. Vol. 6. The Soil Science Society of America, G. G. Pohlman, Treas., Morgantown, West Virginia, 1941. Pp. 521. Price, $5.

This volume contains the 91 papers that were presented at the annual meeting of the Society held in Washington, D. C., November 12–14, 1941, and the minutes of the annual business meeting. Of the topics which were the subjects of

special sessions, the most important are calcium in the soil, minor and secondary elements, available nutrients and methods, phosphate and potash studies, forest influences, and water relationships affecting agronomic practices. A great variety of other topics are also considered. Included among these are papers on soil-forming processes, organic matter, x-ray studies, electron micrographs, organic phosphorus in soils, the hydrogen ion in plant nutrition, rhizobia bacteriophage, color standards, inventory of soil productivity changes, and making agronomic research effective by means of field demonstrations. Every soil science worker will want a copy of this volume for ready reference.

The Stone That Burns. By WILLIAM HAYNES. D. Van Nostrand Company, Inc., New York, 1942. Pp. 345, illus. 58. Price, $3.75.

An exciting story of the development of the sulfur deposits of the United States, in which a vivid picture is presented of the ingenuity of chemical engineers in making available within our borders abundant supplies of this basic chemical raw material so essential to our national welfare, no matter whether we are at war or at peace.

THE EDITORS.

ZINC DEFICIENCY OF PINEAPPLES IN RELATION TO SOIL AND PLANT COMPOSITION[1]

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The early studies on the role of zinc in plant growth showed that the application of zinc compounds to various crops growing in water cultures or in soil caused a toxicity in some instances and a stimulation in others. Brenchley (4), for example, considered zinc to be a plant poison, whereas Javillier (8), and later Allison *et al.* (1), obtained definite growth improvements when several field-grown plant species were fertilized with zinc. It has since been shown that many physiological disorders, such as, the "little leaf" of deciduous fruit trees, "frenching" and "mottle leaf" of citrus, "bronzing" of tung trees, "white bud" of cereal crops, and others are overcome, in many instances, by treatment with zinc compounds. Little is known, however, concerning the zinc concentration of soils and plants in relation to the observed physiological disorders.

Of particular interest, in Hawaii, was the discovery that certain abnormal conditions of pineapple plants could be corrected by spraying with zinc sulfate. The purpose of this investigation was to study the zinc content of pineapple plants and soils in relation to the observed zinc-deficiency symptoms in the field.

POLAROGRAPHIC DETERMINATION OF ZINC IN PLANTS AND SOILS

The common procedures for the determination of zinc as applied to plants and soils have the objectionable features of requiring large samples and of being slow and time-consuming. Little success has been reported with spectrographic methods on these materials.

A polarographic method for the estimation of zinc in plant material was proposed by Stout *et al.* (11). This procedure requires a dithizone separation of the heavy metals prior to the polarographic determination of zinc. Reed and Cumming (10) determined the zinc content of plant material polarographically by the use of a modification of the Stout *et al.* procedure which eliminated the dithizone separation.

Zinc determination in plant tissue

Some preliminary trials with the polarographic determination of zinc in plant tissues indicated that dry ashing, dithizone separations, and filtrations led to

incomplete recoveries of zinc. Hence the following procedure of zinc determination was adopted:

One gram of plant tissue and 15 ml. of concentrated HNO_3 were placed in a 200-ml. high-form beaker, covered with a watch glass, and digested at low heat until the initial rapid oxidation subsided. The heat was then increased to boiling and continued until the contents of the beaker almost reached dryness. The beaker was cooled and 6 ml. of HNO_3 followed by 4 ml. of $HClO_4$ added. The digestion was resumed and the $HClO_4$-HNO_3 mixture refluxed for about 3 hours to ensure complete oxidation of all organic materials. The contents of the beaker were cooled, 1 ml. 10 N HCl was added, and this mixture was refluxed for a few minutes to dissolve any entrained materials deposited on the beaker walls and watch glass. After again cooling, the watch glass and beaker walls were washed with water and the contents taken to dryness. The last traces of $HClO_4$ were removed by brushing the beaker with a Bunsen flame.

The residual salts from the $HClO_4$ digestion were converted to chlorides by three successive evaporations with 5-ml. portions of 10 N HCl. These salts were then taken up in 10 ml. of 0.5 N acetic acid, refluxed for 10 minutes, and the beaker was thoroughly policed to suspend the silica. About 0.2 gm. of finely pulverized metatitanic acid was added and the suspensions swirled intermittently for an hour. This suspension was transferred to a graduated centrifuge tube and diluted to 40.0 ml. with water. The silica and titanic acid were removed by centrifuging, and a 25- to 35-ml. aliquot of the supernatant liquid was siphoned into a 50-ml. flask. This aliquot was slowly taken to dryness at a temperature below boiling, and the last traces of acetic acid were removed by placing the flask in an 80°C. oven for 30 minutes. This residue was dissolved in a measured amount (usually from 5.0 to 10.0 ml.) of electrolyte solution 0.1 N with respect to acetic acid adjusted to pH 4.6 with NH_4OH, and 0.05 N with respect to KSCN. After the residue had been completely dissolved the zinc concentration was determined polarographically.

The above procedure for determining zinc in plant tissue proved to be very satisfactory when applied to the various organs of the pineapple plant. The use of a perchloric-acid digestion eliminated the volatilization or occlusion of zinc within the siliceous materials during a dry-ashing. Piper (9) and Gieseking et al. (6) have discussed the significant losses of bases that may occur.

The addition of metatitanic acid[3] in the procedure was to remove the phosphate present. During the development of the procedure it was found that the phosphate present in the residue (remaining after removal of the silica and acetic acid) prevented the complete dissolving of the zinc salts by the ammonium-acetate–potassium-thiocyanate solution. An incomplete recovery of the zinc resulted if the insoluble phosphates were centrifuged out of the final solution. Tests showed that the metatitanic acid removed at least 95 per cent of the phosphrous without interfering with the zinc concentration.

Zinc determinations in soils

Procedures were perfected for the determination of soil zinc soluble in an ammonium acetate solution (pH 4.6) and in CO_2-saturated water. The choice of these extraction agents was more or less empirical. The use of ammonium acetate is advantageous because zinc-free solutions can be readily prepared

[3] The metatitanic acid was prepared in this laboratory.

from reagents easily freed from heavy metals by distillation. Further, after the extraction is completed the ammonium acetate is eliminated by a simple evaporation. The CO_2-saturated water extraction has similar advantages.

Determination of soil zinc soluble in ammonium acetate. Ten grams of 20-mesh soil and 200 ml. of ammonium acetate solution (N acetic acid, adjusted to pH 4.6 with ammonium acetate) were mechanically shaken for 2 hours. This suspension was allowed to stand overnight and then clarified by centrifuging. A 150-ml. aliquot of this extract was placed in a 200-ml. high-form beaker, evaporated to dryness at 90°C., and the last traces of ammonium acetate removed by twice washing the beaker walls with water and evaporating to dryness. To the beaker were then added 10 ml. of HNO_3 and 1 ml. of $HClO_4$. The beaker was covered with a watch glass and its contents were evaporated almost to dryness at boiling temperatures. The contents of the beaker were cooled, 1 ml. 10 N HCl was added, and this mixture was refluxed for a few minutes to dissolve any entrained materials. The remainder of the procedure was the same as that previously given for plant material, with the exception that it was not necessary to remove the small quantities of phosphorus present with metatitanic acid.

Determination of soil zinc soluble in CO_2-saturated water. Fifty grams of soil and 200 ml. of CO_2-saturated water were shaken mechanically for 2 hours and allowed to stand overnight. The suspension was then clarified by centrifuging, and a 150-ml. aliquot of the supernatant liquid was evaporated to dryness in a beaker. Five milliliters of 10 N acetic acid was added, the beaker policed, and the material suspended and allowed to stand for 15 minutes. The suspension was then transferred to a graduated centrifuge tube diluted to 40 ml., and the insoluble material or colloidal material not eliminated previously, removed by centrifuging. A 35-ml. aliquot of the supernatant liquid was evaporated to dryness. The organic matter was removed by adding 4 ml. of HNO_3 and 1 ml. of $HClO_4$, covering with a watch glass, and boiling until near dryness. One milliliter of HCl was added and allowed to reflux for a few minutes. After cooling, the beaker walls and watch glass were rinsed, the contents taken to dryness, and the last traces of $HClO_4$ removed by brushing the beaker with a Bunsen flame. The residual salts were converted to chlorides by three successive evaporations with 5-ml. portions of 10 N HCl. These chlorides were dissolved in 2 ml. of ammonium acetate-potassium thiocyanate electrolyte solution, and the zinc was determined polarographically.

ZINC CONTENT OF PINEAPPLE SOILS AND PLANTS

The leaves of pineapple plants growing in various parts of Hawaii have, on occasion, shown symptoms of physiological disorders that can be corrected by spraying with zinc sulfate. There are apparently two phases of this disorder. The more common and less severe is a mottling and blistering of the upper surfaces of the leaves, illustrated in figure 1. On occasions, the younger leaves of the heavily mottled plants are unmottled but show a marked curvature which apparently occurs as a secondary symptom of zinc deficiency. Severe curvature is illustrated in figure 2, in comparison with normal, uncurved "heart" leaves in figure 3. Plants that exhibit this leaf curvature produce fruits or secondary growth only after considerable delay.

In order to study the relationships between zinc in pineapple soils, its absorption by the plants growing in them, and the symptoms exhibited, where deficiencies occur, collections were made of plant and soil samples covering a wide range of variations. The following empirical classification of the appearance

FIG. 1. ZINC-DEFICIENCY SYMPTOMS OF PINEAPPLES—MOTTLING AND BLISTERING OF UPPER
SURFACES OF LEAVES

Left to right, the leaves are alternately unmottled and mottled

of the plants was adhered to as closely as possible in describing the samples
taken for the purposes of this investigation:

Zinc-deficiency index	Plant appearance
0	Normal.
1	*Slight mottling:* Appearing as a symptom of incipient deficiency, which often disappears with further growth. It may be incident only after blossoming.
2	*Medium mottling:* A significant deficiency usually incident before blossoming.
3	*Heavy mottling:* Often incident before the red-bud stage.
4	*Very heavy mottling:* Usually incident in the initial stages of growth shortly after planting, causing a delayed fruiting. Fruits may be abnormal.
5	*Curvature of leaves:* Appearing after the very heavy mottling stage described in 4, above. Fruiting is greatly delayed.

Ballard and Linder (2), Barnette and Warner (3), Haas (7), and others, have indicated that symptoms of zinc deficiency appear at various stages of growth and become more pronounced under certain weather conditions, or upon changes in the metabolic status of the plants (5). Similar variations of the incidence of deficiency symptoms have been noted with pineapples. Thus, wherever possible, the classification of the samples was based on the knowledge of previous as well as current crop cycles. Where little knowledge of the previous cycles was available, the samples were judged by the appearance of the plants in the area at the time of sampling.

FIG. 2   FIG. 3

FIG. 2. ZINC-DEFICIENCY SYMPTOMS OF PINEAPPLES—SEVERE CURVATURE OF "HEART" LEAVES, A SECONDARY PHASE OF THE PHYSIOLOGICAL DISEASE ILLUSTRATED IN FIGURE 1

FIG. 3. NORMAL PINEAPPLE "HEART" LEAVES

All soil and plant samples were taken from areas that had received no zinc fertilization. Where plant samples were taken and composited, the corresponding soil samples were obtained and composited from the positions immediately under the plants removed.

Soil composition and zinc-deficiency symptoms

Nineteen soil samples were collected from widely separated pineapple areas known to have shown symptoms of varying degrees of zinc deficiency. These samples were in each instance representative of the surface 12 inches of soil.

The soil zinc soluble in both ammonium acetate (pH 4.6) and CO_2-saturated water was determined by the methods described above. A comparison of these determinations with the observed degree of zinc-deficiency symptoms shown by pineapple plants growing on the soils is given in table 1. An interesting relationship is evident between the soil zinc extracted by the ammonium acetate solution and the indexes of deficiency exhibited by the crops. The outstanding

TABLE 1

Relationship of soluble soil zinc to indexes of zinc deficiency exhibited by pineapple plants growing in these soils

SAMPLE NUMBER	SOIL pH	ZINC-DEFICIENCY INDEX	SOIL ZINC SOLUBLE IN AMMONIUM ACETATE AT pH 4.6	SOIL ZINC SOLUBLE IN CO_2-SATURATED WATER
			p.p.m.	*p.p.m.*
12	4.9	0	3.5	0.11
14	5.6	0	3.1	0.05
2	4.1	0	2.6	0.21
13	4.5	0	2.2	0.08
10	4.3	0	1.7	0.14
Mean..........	4.7	..	2.6	0.12
15	5.6	1	1.5	0.03
11	4.3	1	0.8	0.06
17	4.0	1	0.7	0.13
Mean..........	4.6	..	1.0	0.07
1	4.0	2	1.4	0.11
6	5.4	2	1.0	0.03
19	4.7	2	0.9	0.08
Mean..........	4.5	..	1.1	0.07
5	5.9	3	3.9	0.05
4	4.4	3	0.8	0.06
3	4.3	3	0.6	0.05
Mean..........	4.9	..	1.8	0.05
7	4.4	4	0.6	trace
16	4.3	5	0.6	trace
9	5.5	5	0.6	trace
8	4.3	5	0.5	0.02
18	4.2	5	0.5	0.03
Mean..........	4.6	..	0.6	0.01

discrepancy is that shown by soil sample 5, which contained a large amount of available zinc although the plants growing on it appeared to be zinc-deficient.

Although in some extracts there were also measurable quantities of lead and nickel, this study was confined solely to zinc, and the possible significance of other heavy metals was not considered.

The relation between the soil zinc soluble in CO_2-saturated water and the severity of zinc-deficiency symptoms is not clearly defined. Apparently the

soil pH affects the solubility of the zinc in the CO_2-saturated water, the solubility being lower at the higher pH values.

Plant composition and zinc-deficiency symptoms

In order to study the possible relationships between plant composition and the zinc-deficiency symptoms, nine sets of pineapple plants showing the various degrees of zinc deficiency were collected and analyzed for their zinc content.

The plants in each set were arbitrarily divided into groups[4] of comparable physiological development. All leaves that were fully or partly grown at planting time (classed as A and B leaves) were discarded, and the remaining leaves segregated as follows:

C—Fully grown leaves at an angle of more than 45° from the vertical;
D—The longest fully grown leaves, or those 30–45° from the vertical;
E—The leaves more than foot long and less than 30° from the vertical;
F—The remaining leaves and leaf primordia.

Each group of leaves was then divided into three portions as follows: the basal, white meristematic tissue; the central portion or that between the white meristematic tissue and the region where the leaves begin to taper to a point; and the remaining portions or tips. The top inch of each stump was considered to be the growing point.

Leaves of fruiting plants were segregated as above, but the last leaves formed were placed in the E rather than the F group. These included the leaves on the peduncle. Only the "shells" of fruits were kept for analysis. Two methods were used to segregate secondary growth. In sets I and V all crowns, slips, and suckers were composited, whereas in set VI the crowns were analyzed separately.

The zinc concentration in the plant tissues was determined by means of the polarographic procedure. The results are presented in table 2. An examination of these data shows the highest concentrations of zinc to be in the meristematic tissues, i.e., growing points and white basal leaf tissues. The concentration of zinc in the growing points appears to be closely related to the observed deficiency symptoms. The severely zinc-deficient plants (plants VIII and IX) had a low amount of zinc in all meristematic tissues.

Had it been possible to study plants of comparable ages which had been grown under similar environmental conditions, the relationship of the degree of zinc-deficiency symptoms, the plant composition, and the soil composition might have been more satisfactory.

Although the possibility of using the concentration of zinc in the growing points of the pineapple plants presents itself as a means of diagnosing zinc deficiency, this technique is hardly adaptable to practical agriculture.

These data indicate that the deficiency symptoms which are corrected by the spraying of zinc sulfate solutions on pineapple plants are associated with an

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[4] This system was adopted upon the suggestion of C. P. Sideris, Pineapple Research Institute of Hawaii.

TABLE 2

Zinc content of soil and of the various parts of several sets of pineapple plants

PLANT SET NUMBER	GROWTH STATUS	SOIL ZINC	ZINC DEFICIENCY INDEX	ZINC DETERMINED IN SEGREGATED TISSUES *														
				C Leaves			D Leaves			E Leaves			F Leaves	Growing points	Fruit shell	Crowns only	Slips and suckers only	Crowns, slips, and suckers
				Basal	Central	Tips	Basal	Central	Tips	Basal	Central	Tips	Entire					
		p.p.m.		p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
I	1st ratoon, with fruit 3 months after blossoming	2.6	0	44	17	22	44	26	24	42	19	23			21			33
II	Plant crop, 12-month slip planting (hold overs)	3.5	0	20	9	7	25	8	6	23	10	8	27	158				
III	Plant crop, 10-month slip planting	1.7	0	16	6	4	16	9	12	24	13	10	28	144				
IV	Plant crop, 16-month slip planting (hold overs)	0.8	1	20	8	4	20	11	7	26	13	9	22	96				
V	1st ratoon, with fruit 3 months after blossoming	0.9	2	22	15	10	21	14	15	26	17	26			26			27
VI	Plant crop with fruit 3 months after blossoming	0.6	3	21	8	4	19	8	6	16	7	5			20	17	12	
VII	1st ratoon, suckers, no evidence of red-bud	3.9	3	21	10	5	21	11	6	16	13	10	21	81				
VIII	Plant crop,† 12-month crown planting	0.6	4	7	5	8	8	5	8	13	6	8	12	23				
IX	Plant crop,† 12-month crown planting	0.5	5	4	8‡		7§	6‖						6				

* All analyses of plant tissues given on the dry basis.

† Hilo Cayenne variety. All others were Smooth Cayenne.

‡ Combined C central and tips.

§ Combined D, E, F basal.

‖ Combined D, E, F central and tips.

insufficient concentration of the micronutrient in certain tissues of the plant. Although the D leaves are the ones that most readily show the symptoms of zinc deficiency, there is no relation between the concentration of zinc in these leaves and the degree of zinc deficiency.

From these limited data, however, it may be concluded that there exists a definite correlation of available soil zinc, of the zinc found in the growing-point tissues, and of the symptoms of zinc deficiency exhibited by the plants.

SUMMARY

A rapid, direct procedure for the polarographic determination of zinc in pineapple plants was developed. The essential features of this procedure are a wet combustion followed by the removal of phosphate by absorption with metatitanic acid.

A procedure for determining the soluble zinc in soils is proposed.

A relationship apparently exists between the degree of zinc deficiency exhibited by pineapple plants and the soil zinc soluble in ammonium acetate at pH 4.6.

A study of the distribution of zinc throughout pineapple plants revealed that the meristematic tissues contained the greatest concentrations of zinc. The growing points of zinc-deficient pineapple plants were found to contain less zinc than normal or slightly zinc-deficient plants and to be related to the degree of zinc deficiency.

Apparently the abnormalities of pineapple plants cured by spraying with zinc sulfate are a direct result of the inability of the soil to supply sufficient zinc to the plants.

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SOIL PROPERTIES OF TILLED ORCHARDS COMPARED WITH UNTILLED AREAS

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It is well known that long-continued cultivation and cropping may result in profound changes in both physical and chemical properties of the soil. In many instances, changes that are quite apparent under careful observation, are elusive and difficult of measurement. This is particularly true of changes in physical properties, such as soil structure as it is related to porosity and permeability. The data in this paper are presented to indicate significant differences in properties of soils that have been subjected to much cultivation in orchard management compared to the properties of similar soils that have not been cultivated.

EXPERIMENTAL METHODS

The methods used have been presented, for the most part, in previous publications (6, 7). In this study, the apparent specific gravity of thin layers of soil was determined by studies of essentially undisturbed samples taken by the use of a metal rim 2 inches deep and 6 inches in diameter. One side of the rim has a cutting edge to aid in penetrating the soil. The use of a shallow rim made it possible to sample thin layers, such as might be found where tillage pans have developed. The rim is pressed into the soil layers to be sampled, then dug out and sliced smooth on both faces with a long knife. The sample of soil thus obtained is exactly the volume of the rim, and has its natural structure virtually undisturbed. From measurements of the real specific gravity and of the volume weight corrected for moisture, the total porosity of these samples is calculated. Capillary porosity is obtained from the pore space occupied by water at field capacity. Samples taken in the field within 48 hours after the soil has been thoroughly wet and the gravity water has disappeared are assumed to be at field capacity. The noncapillary porosity is the difference between total and capillary pore space.

SOILS STUDIED

Most of the soils used in this study were supporting walnut or filbert orchards 20 to 30 years old. The orchards have been either continuously clean-cultivated or winter-covercropped and summer-cultivated. Samples representing the un-

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cultivated soil were usually taken from fence rows or from roadsides where the
natural vegetation, grass or a combination of grass and weeds, has been undis-
turbed for a number of years.

Both the cultivated and the uncultivated soils of this study were under grass
previous to the arrival of early settlers some 75 to 100 years ago. Early settlers
picked the grass areas for their farm sites largely, perhaps, because little clearing
for the plow was necessary. It cannot be assumed, however, that the orchard
soils under study were once similar in physical and chemical properties to the
uncultivated fence-row soils with which they are compared, since in all prob-
ability the soils of the fence rows have also changed because of the accumulation
of eroded soil in the grass area, differences in the control of fire, grazing by live-
stock, and other pertinent factors.

The Willamette is an old valley-filling soil, of good quality, and supporting
good orchards. The Aiken and Olympic soils are hill formations derived from
igneous rocks. The Melbourne is a hill soil derived from sedimentary rocks,
sandstone, and shale. The Newberg is a recent river bottom soil, usually very
productive under irrigation. These soils have been described in previous work
(5, 6) and in the soil survey reports for Washington County and the Eugene
Area (3, 11).

The Melbourne soil is subject to erosion when left bare by cultivation. It is
found on slopes and lacks binding material to form stable nonerodible granules.
The Willamette soil is usually only gently sloping and not subject to much ero-
sion. Humus depletion due to tillage in some soils has been very appreciable.
Some of both the Aiken and the Melbourne soils have been long cultivated.

RESULTS OF STUDY

Organic matter depletion to a lower semistable equilibrium level is the natural
consequence of the destruction of the virgin sod. Where erosion occurs, deple-
tion is more rapid and more severe. The data of table 1 indicate the difference
in organic matter content (10) of several soils that have been under cultivation
for varying lengths of time. These cultivated soils contain from one fifth to two
fifths less organic matter than do the adjacent uncultivated fence-row soils.
No erosion measurements were made, though it is known that some erosion has
occurred, particularly on the Melbourne soils and on the steeper slopes of the
Aiken. In some soils, such as Aiken clay loam II, organic matter in the surface
6 inches of soil may be more than 50 tons an acre.

The organic matter in the upper 3 feet of good soil of the types studied com-
monly amounts to 75 to 150 tons an acre, and contains 4 to 8 tons of nitrogen
(7). Since nitrogen and organic matter run parallel, a loss of one third of the
organic matter, assuming that the change occurs to the 3-foot depth, may mean
a difference of 3,000 to 6,000 pounds of nitrogen an acre. This difference is
serious, as the nitrogen is gone beyond recovery. That the deep soil contains
little nitrogen is indicated by the low organic matter content (6, 7) in contrast
with the supply of minerals, which in some instances is larger than in the sur-
face. Organic matter loss is, therefore, more serious than loss of mineral matter,
which is more or less abundant in the subsoil.

Soil impoverishment is often attributed to the depletion of available nutrients. Some decrease in available phosphorus (9) is shown by the data of table 2. The supply of available phosphorus in these soils is relatively low.

TABLE 1

Soil organic matter in uncultivated and in cultivated soils

0–6-inch depth

SOIL	ORGANIC MATTER			YEARS OF CULTIVATION
	Unculti-vated fence row	Cultivated orchard	Difference	
	per cent	*per cent*	*per cent*	
Willamette silt loam I...............	4.08	2.45	40.0	General farm 50 ? Orchard 25
Melbourne silt loam I...............	4.08	2.75	32.6	15
Willamette silt loam II..............	4.04	3.09	23.5	......
Soil unclassified, The Dalles.........	2.86	2.21	22.7	Unknown
Aiken clay loam I....................	4.20	2.41	42.6	......
Melbourne loam I....................	3.01	1.80	40.2	Grain 50 Orchard 32
Aiken clay loam II..................	5.37	4.17	22.3	Grain 60 Orchard 30
Olympic clay loam..................	3.23	2.24	30.7	Orchard 30
Melbourne loam II..................	3.74	2.21	41.0	Grain 30–50 Orchard 30
Average..........................	3.84	2.59	33.6	

TABLE 2

Available phosphorus in cultivated and in uncultivated soils*

DEPTH	AVAILABLE PHOSPHORUS							
	Soil unclassified		Soil unclassified		Newberg sandy loam		Melbourne clay loam	
	A	B	A	B	A	B	A	B
inches	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*	*p.p.m.*
0–6	240	150	300	250	100	100	99	71
6–12	200	150	272	230	84	125	36	24
Average..............	220	150	286	240	92	113	68	48
Percentage difference as of uncultivated..		−31.8		−16.1		+22.8		−29.4

* A = uncultivated; B = cultivated. Data from Truog (9).

The data indicate a decrease in available phosphorus in three soils and an increase in the fourth. The increase in available phosphorus in the Newberg soil may have resulted from small amounts of farm manure known to have been used in the past. There is no record of any treatment that would add phosphorus to any of the other soils.

Available phosphorus determined by chemical methods (9) is frequently of the order of 100 pounds per acre for the 3-foot profile in the red hill soils in contrast to 1500 or more pounds in some of the more fertile river bottom and valley floor soils (7).   This low availability in the hill soils is probably not entirely the result of cropping but is due to certain fundamental soil properties such as high acidity and fixation of phosphorus by iron and aluminum or perhaps by the colloidal clay (2, 4).   Available phosphorus in the hill soils as indicated by crop growth is higher than that shown by chemical methods (7).   Cultivation in itself, for a time at least, increases the availability of nutrients.   A cultivated

TABLE 3

Effect of cultivation on organic matter depletion and on physical properties of Aiken clay loam

HORIZON	APPARENT SPECIFIC GRAVITY	TOTAL POROSITY VOLUME	CAPILLARY POROSITY VOLUME	NON-CAPILLARY POROSITY VOLUME	WEIGHT PER CU. FT.	ORGANIC MATTER CONTENT
inches		*per cent*	*per cent*	*per cent*	*lbs.*	*per cent*
Uncultivated soil						
0–2	0.91	65.7	41.8	23.9	56.8	7.85
3–5	1.05	60.5	37.2	23.3	65.6	4.45
6–8	0.97	63.2	34.2	29.0	60.6	2.58
Average	0.98	63.2	37.7	25.4	61.1	4.96
Cultivated orchard—30 years old						
0–2	1.29	51.5	38.2	13.3	80.6	3.33
3–5	1.34	49.6	37.6	12.0	83.7	2.89
6–8	1.30	51.1	37.5	13.6	81.2	2.89
Average	1.31	50.7	37.8	13.0	81.8	3.04
Percentage difference as of uncultivated...	+33.7	−19.8	+0.26	−48.8	+33.9	−38.7

crop, therefore, may show a higher availability of phosphorus than the chemist would report.

The depletion of organic matter from soils under tillage is commonly associated with a soil structure breakdown.   Soil life is reduced and the granules disperse, the soil runs together when wet and bakes or cements when dry.   Because of the change in structure and porosity, the soil under cultivation comes to have a high volume weight.   These changes in Aiken soil are brought out in the data of table 3.

The uncultivated soil was taken from a roadside fence row and was supporting a dense grass sod.   The cultivated orchard sample was from a similar soil that had been cropped to grain for half a century before the orchard was planted.

The orchard is now 30 years old and the trees are about half the size of those of similar age on the best soils. The apparent specific gravity has increased and the total porosity has decreased as a result of long tillage. The decrease in porosity results from the disappearance of about half the larger (noncapillary) pores. The decrease in organic matter has been in the surface 5 inches of soil. These data are illustrative of the drastic soil changes that may be brought about by long-continued tillage and organic matter depletion, on the one hand, and by continued growth of vigorous grass with its dense mat of roots and protective cover, on the other hand.

TABLE 4

Effect of tillage and of elimination of surface plant cover on the physical properties of Newberg silt loam

HORIZON	APPARENT SPECIFIC GRAVITY	TOTAL POROSITY VOLUME	CAPILLARY POROSITY VOLUME	NONCAPILLARY POROSITY VOLUME	WEIGHT PER CU. FT.
inches		per cent	per cent	per cent	lbs.
Uncultivated soil					
0–2	0.98	63.0	33.1	29.9	61.2
4–6	1.02	64.7	34.9	29.8	63.7
7–9	0.91	65.7	33.1	32.6	56.8
Average	0.97	64.5	33.7	30.8	60.6
Cultivated orchard					
0–2	1.36	48.9	48.7	0.2	85.0
4–6	1.33	50.0	46.4	3.6	83.1
7–9	1.12	57.7	44.0	13.7	70.0
Average	1.27	52.2	46.4	5.8	79.4
Percentage difference as of uncultivated...	+30.9	−19.1	+37.7	−80.5	+31.0

The Aiken soil, in the uncultivated state, is granular and porous. Little or no run-off of water and no soil erosion occur for some time after it is placed under cultivation. The orchard soil from which the data of table 3 were obtained has reached a condition in which the infiltration capacity is limited. During heavy prolonged rains, there is considerable run-off and on the steeper slopes serious erosion has taken place.

Melbourne soils long under cultivation run together to a greater degree than do the Aiken soils. In some old grain fields the Melbourne soil has become so cemented in the entire cultivated depth that a chunk fractures from a compact zone like a piece of stone. One such soil[2] was so compacted that it weighed

[2] Unpublished data.

nearly 95 pounds per cubic foot, whereas soils with the best spongy structure weigh not more than 75 to 85 pounds per cubic foot.

In some soils the effect of continued tillage is most noticeable immediately below the soil surface, particularly if the surface soil is of heavy texture and is unprotected by vegetation. This condition is shown in cultivated Newberg silt loam (table 4), in which the surface 2 inches are nearly completely sealed. The soil in the lower depths becomes sandy and permeable. The soil when irrigated holds water on the surface in the depressions, sometimes for several days. Since this soil in some places has developed a compact layer just below the tillage depth, probably the impermeability to water is due to the combined effect of the dispersed and sealed surface and the tight tillage pan.

The breakdown of structure in this soil is most noticeable in the top 2 inches. Three profiles studied showed the same condition. This soil has lost nearly its

TABLE 5

Some physical properties of the different layers of the soil profile—Willamette silt loam, cultivated

HORIZON	APPARENT SPECIFIC GRAVITY	TOTAL POROSITY VOLUME	CAPILLARY POROSITY VOLUME	NONCAPILLARY POROSITY VOLUME	WEIGHT PER CU. FT.
inches		*per cent*	*per cent*	*per cent*	*lbs.*
0– 2	1.37	48.5	36.3	12.2	85.6
3– 5	1.38	48.1	30.6	17.5	86.3
7– 9	1.49	44.0	33.1	10.9	93.1
10–12	1.32	50.3	36.3	14.0	82.5
14–16	1.25	53.0	35.3	17.7	78.2
17–19	1.26	52.1	36.8	15.3	78.8
20–22	1.36	48.6	35.8	18.8	85.0
23–25	1.33	50.4	40.6	9.8	82.2
26–28	1.29	51.8	41.7	10.1	90.6

entire noncapillary porosity in the immediate surface, thus retarding the exchange of gases when the soil is wet. Soils of this type are commonly under irrigation. In this particular orchard there has been trouble at times from premature leaf fall and shriveled kernels of walnuts. There may be a connection between the condition of the soil and the behavior of the trees. Since irrigation water is applied in warm summer weather, the temporary interference with soil aeration may be in part responsible for the unsatisfactory responses of the walnut trees.

The presence of tillage pans in many of the cultivated orchards can be easily observed. The pan layer may have the appearance of a cemented slab of earth, which can be removed. A measurement that will indicate satisfactorily the extent of the structure change which has occurred is difficult to obtain. The data of table 5 indicate the properties of the different layers of soil in a typical Willamette silt loam profile.

In this Willamette soil the typical pan layer is at the 7–9-inch depth. The

pan is compressed and cemented and usually is more noticeable in the fall after the tillage season and about the time rains begin. The soil softens with the rains first above and then below the pan to a greater extent than in the pan layer. Porosity, particularly the noncapillary, is reduced and the density is increased in the pan layer. Generally, the most porous layer is below the pan, indicated in this soil at the 14–19-inch depth. This layer is very permeable and is spongy, full of cavities, and undisturbed by tillage. The better structure is indicated by the reduced density of the soil and the greater noncapillary porosity. The appearance and feel of the soil indicate a greater difference in the different layers than the data indicate. The condition of the cultivated layer of soil depends in part upon time elapsed and amount of rain since the last cultivation.

Tillage in preparation of a seedbed creates a temporary good physical condition, which disappears and shows the real change in the soil structure that has been brought about only after rains have caused the soil to run together. This soil at the time of sampling had not yet run together in the cultivated horizon to nearly so great an extent as had Newberg silt loam of table 4. The pan layer, however, was very evident.

The properties of the pan in contrast to those of the more porous layers under the pan are brought out by following the percentage increases or decreases of the most cemented pan calculated from the data in table 5 for the 7–9-inch and the 14–16-inch depths: apparent specific gravity, $+16.1$; total porosity volume, -20.5; capillary porosity volume, -6.6; noncapillary porosity volume, -62.4; weight per cubic foot, $+16$. The decreased noncapillary porosity and the increased volume weight in the pan compared with the porous layer are significant. This is a characteristic condition of orchard soils in western Oregon.

The presence of the porous layer under the pan first became evident during sampling with the King tube. Considerable pounding was necessary to force the tube through the tillage pan. When the porous layer was reached the tube would drop several inches from a single stroke. This contrast in the different soil layers is the rule rather than the exception in the orchard soils studied. Even when measurements indicate much smaller differences than are presented here, the contrasting appearance and feel of the different layers are marked.

DISCUSSION

After the use of both chemical and physical methods of study of many soils it is evident that some significant changes brought about by cultivation are associated with organic matter depletion and a change in soil structure. Chemical differences are often entirely inadequate to account for differences in productivity. Even where erosion does not occur, continuous clean cultivation of the soil for crop production in orchards brings about disastrous changes in physical soil properties.

The most pronounced soil structure changes are evident in the immediate soil surface and in the tillage pan just below the depth of tillage. Both layers, the surface and the tillage pan, may become nearly impermeable to water. Un-

desirable physical properties found at a depth of 3 to 5 feet in the soil are princi-
pally the result of long-time processes (5) and are perhaps little influenced by
tillage and management.

Low availability of phosphorus is rather common on some of the less produc-
tive soils and is influenced by cropping and fertilizer practice. A fertilizer and
manuring program might easily return more phosphorus to the soil than crops
remove. One hundred pounds of 16 per cent superphosphate yearly would re-
place the phosphorus removed by 25 bushels of wheat in the grain and the straw.
Removal of 50 crops of 20 bushels of wheat, or a total of 1,000 bushels an acre,
has been estimated on some areas previous to the planting of an orchard. This
grain and straw would remove about 300 pounds of phosphorus an acre. Re-
moval is not confined to the top foot of soil, however, and the difference in avail-
able phosphorus remaining in the surface soil might be much less than the total
crop removal, as many data indicate, even when no fertilizer has been used.
Doubtless, some phosphorus is taken from the deep soil by the growing crops.

A depletion of organic matter, besides being associated with physical and
chemical deterioration, results in unfavorable biological changes in the soil.
Albrecht (1) has shown that nitrates may be 3 months later in appearing in soils
depleted of organic matter, and may be at a much lower level when they appear.
This is indicative of the slowing down of biological processes and a consequent
reduction in availability of all nutrients obtained from the soil. The increased
use of commercial fertilizers, not only for orchards but for all crops, is evidence
of increasingly deteriorated soils. Fertilizers applied to correct chemical defi-
ciencies will not maintain soils with desirable physical properties for maximum
production. When used to grow humus materials, fertilizers have their greatest
value for soil improvement. Stevens (8) stresses the importance of humus re-
newal not only for supplying nitrogen but for maintaining favorable physical
properties in the soil.

Soils need periods of rest from tillage in order to grow soil-building plants
for physical reasons, as much as rest from removal of nutrients. Soils usually
develop their highest level of productivity under a vegetative cover undisturbed
by plows or other implements. These same soils when devoted to agricultural
uses must have periods of recuperation under a vegetation selected, planted,
and fertilized for good growth. The tendency of orchardists in some sections
to cease cultivation and to return their orchards to permanent sods is a recogni-
tion of these fundamentals.

Organic matter content on a percentage basis may not be a reliable indication
of fertility. Some of the old depleted soils contain considerable organic matter.
The value of organic matter seems to be determined as much by its activity as
by the amount present. Some of the old hill soils of low productivity may con-
tain more organic matter than the recently formed and very productive river
bottoms. Crop yields depend on the presence of biologically active organic
matter and high availability of nutrients. Since the organic matter content
of some of the hill soils is relatively high, whereas yields are relatively low, it is

assumed that the organic matter is old and resistant rather than biologically active, perhaps from both physical and chemical causes.

Fresh composts, farmyard manure, and green manures are very stimulating to plant growth as they decompose in the soil.   Regular and consistent renewal of the organic matter results in good plant growth.   In fact, it is essential to maintain a responsive soil.   Roots foliage residues, and insect and other animal life in nature contribute to the development of the chemical, physical, and biological soil environment most favorable to plant growth.   To place land under cultivation is to subject the soil to a new set of influences, not all of them favorable to the maintainance of the desirable properties that nature has previously developed.   The ordinary tiller of the soil, while not forgetting the importance of good tools and proper tillage at the right time, needs also an appreciation of the limitations of tillage tools and a proper conception of the possible derogatory changes which occur in soil after long periods of too-continuous tillage and organic matter depletion.

CONCLUSIONS

Some cultivated orchard soils in western Oregon contain one fifth to two fifths less organic matter than do similar uncultivated soils.

Availability of phosphorus based upon chemical methods may be reduced as a result of long-continued cultivation, partly through nutrient and organic matter depletion and the unfavorable biotic changes that have taken place.

An appreciable change in soil structure is associated with tillage and organic matter depletion.

Tillage pans that interfere with water penetration and with proper functioning of the soil are common in cultivated orchards.   The immediate soil surface may become dispersed and run together until water cannot penetrate.

Many soils are more spongy and porous a few inches below the depth disturbed by tillage than in any other part of the profile.   This layer is full of large easily visible cavities, probably the result of undisturbed insect and other animal life in the soil.

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SOILS IN A VIRGIN HEMLOCK-BEECH FOREST ON THE NORTHERN ALLEGHENY PLATEAU

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Exploring the relationships between forest soils and the associations of forest trees growing on them is a subject that closely concerns those soil scientists engaged in naming and mapping soil types for field use. The land manager or practicing forester who expects to use these soil surveys as a basis for forest management plans must also have a knowledge of these relationships.

As a result of a study of 15,000 sample plots taken on areas covered by soil surveys, Roe[2] found that many of the more than 400 soil types recognized by surveyors in the Great Lakes region were related to certain broad forest cover types. The northern hardwood forest cover type occurred on 63 of these soil types, or on more different individual soils than any other type of forest in this region. In different soil survey areas, however, Roe found that 14 of the commonly recognized soil types supported different forest cover types. He also listed 18 soil types that support forest vegetation recognizable as belonging to two distinct forest cover types, though occurring in the same locality or soil survey area. In order to simplify the use of soil surveys in forest practice, a search was made for some of the underlying factors controlling the character of the forest. Soil moisture relationships proved to be the answer in the Lake States region, and it was found possible to arrange the 400 soil types into 14 groups of value to the forester. The soil types of each group had common soil moisture characteristics dependent chiefly on the texture of the surface layer, the nature of the subsoil (drainage), and the relative depth of the water table. For each of the 14 soil type groups, it was possible to predict with reasonable accuracy the type of forest most suitable to a given site. Some differences in cover types were noted in the Lake States region due to climatic differences, which must also be taken into account. The same classification of forest soils based on soil moisture relationships was also found to be related to the rate of growth or productivity of the forest trees, since not only cover type, but growth rate on a given site, is determined largely by the moisture relationships of soils.

Quite independent of the extensive studies carried out on the relationships of soils in the Lake States are a series of studies made by the Allegheny Forest Experiment Station in cooperation with the Pennsylvania State College[3], on the

soils and virgin timber types found in northwestern Pennsylvania. An area of some 934 acres lying along the East Branch of Tionesta Creek in Warren and McKean Counties was mapped in detail both as to soil types and as to vegetative cover. As a follow-up of this survey, a series of 10 sample plots, selected for analysis of the age history of the three major forest associations found in various parts of the entire tract of 6,000 acres, were intensively studied in 1934–1935. Analyses were made of soil texture, acidity, loss on ignition, and the readily available mineral nutrients. These plot data will be presented in another article.

Three major soil types, Cookport silt loam, Leetonia stony loam, and Dekalb stony silt loam (steep phase), were encountered (fig. 1). The field notes by Patrick and Garstka[4] indicate that Cookport silt loam and Leetonia stony loam are somewhat similar in origin. Both are true podzols; both are residual soils;
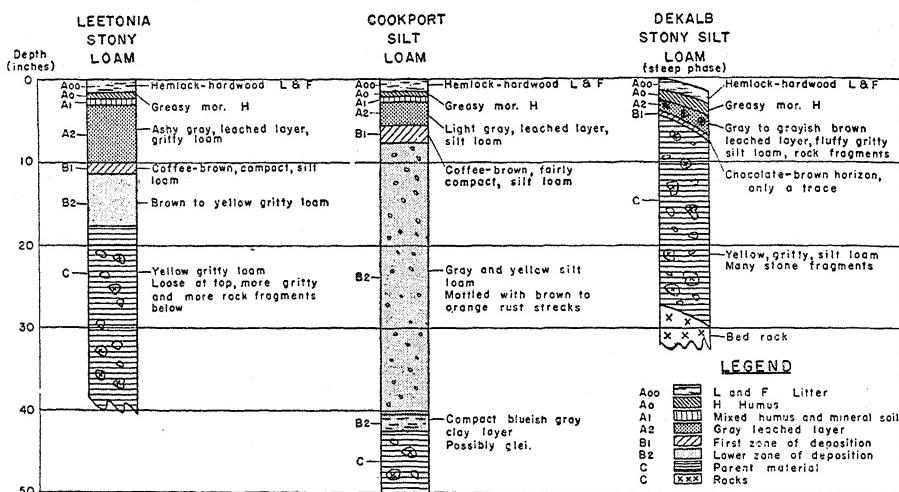
FIG. 1. SOIL PROFILE DIAGRAMS, EAST TIONESTA VIRGIN FOREST

and both occur at the higher elevations. They differ chiefly in that the Cookport is residual from sandstone and shale, the Leetonia from sandstone alone. The Cookport is imperfectly drained, has a perched water table and a compact clay loam horizon 3 to 4 feet below the surface similar to the glei or "gley" layers discussed by Wilde[5]. Leaching of the upper mineral soil layer is much more complete and extends to greater depth in the Leetonia than in either the the Cookport or the Dekalb. There is no mottling or other evidences of improper drainage in the B or C horizons of Leetonia stony loam. In contrast to the Cookport and the Leetonia soils is Dekalb stony silt loam (steep phase),

[4] Patrick, A. L., and Garstka, W. U. 1932 Soil Survey of East Tionesta Virgin Timber Tract. (Mss. report in files of Allegheny Forest Experiment Station.)

[5] Wilde, S. A. 1940 Classification of gley soils for the purpose of forest management and reforestation. Ecology 21: 34–44.

which is found on the steep middle and lower slopes below the general plateau level. It is a well-drained colluvial soil derived from mixtures of shale sandstone and conglomerate. The B horizon is entirely absent or at best present only as a streak a fraction of an inch thick. Although all three soils have sandstone as parent material, and are similar in having an acid "greasy mor"[6] type of humus beneath this hemlock-beech virgin forest, the Cookport is derived partly from shale and the Dekalb from both shale and conglomerate rocks. Genetically, the Dekalb must be classed as an immature soil, the Cookport and Leetonia as mature.

The virgin forest growing on these major soil types was studied in detail, quite independently of the soil type mapping of 1932, the field work being done by an entirely different group in 1930. In 1930, a 5 per cent strip cruise of 1,200 acres having been made part of the 6,000-acre East Tionesta virgin forest about to be logged[7]. An analysis of these field tallies was made, using the relative topographic location of the tenth-acre cruise plots as the basis for describing the virgin stand conditions[8]. The items compared for lower slopes, middle slopes, and upper slopes or plateau top sites, included (a) percentage species composition (abundance) of the dominant stand expressed as number of stems 10 or more inches d.b.h.[9] per tenth acre, (b) frequency of occurrence in percentage of the total of 587 tenth-acre plots sampled, (c) number of d.b.h. size classes represented (five groups), and (d) the stocking expressed as basal area in square feet per acre of the dominant stand. This ecological cruise proved the remarkable uniformity of the virgin hemlock-beech climax forest association, regardless of elevation or relative topographic location, in that limited north slope and plateau portion of the virgin forest covered. Later studies on the south-facing slopes above the main creek show that a severe forest fire in 1644 brought in an even-aged stand of old growth white pine and hemlock, but this forest type was not covered in the publication by Hough.

ANALYSIS OF DATA

With the aforementioned basic data, it seemed possible to make an office check to determine whether any statistically significant difference existed in the character of the virgin forest growing on these three distinctly different major soil types.

The detailed soils map prepared by Patrick and Garstka was used as a base,

[6] Heiberg, S. O., and Chandler, R. F. Jr. 1941 A revised nomenclature of forest humus layers for the northeastern United States. *Soil Sci.* 52: 87–99.

[7] An area of 4,131 acres of this virgin forest, known as the Tionesta Natural and Scenic Area, was purchased by the Federal Government in 1936 and will be preserved for its educational, inspirational, and scientific value.

[8] Hough, A. F. 1936 A climax forest community on East Tionesta Creek in northwestern Pennsylvania. *Ecology* 17: 9–28.

[9] The abbreviation d.b.h. is used for "diameter at breast height." Breast height refers to a point of measurement 4.5 feet above the average ground level.

the positions of all tenth-acre strip plots, accurately located in 1930, being super-imposed on the various soil types mapped[10]. Of the 492 tenth-acre strip plots which fell within the 934-acre tract covered by the soil type map, a total of 99 were crossed by the boundary lines between soils or were within one-half chain of such soil type lines. These 99 plots were arbitrarily rejected to avoid possible errors in assigning these border line plots to given soil types. The remaining 393 tenth-acre plots fell within the three major soil types as follows: 192 in Cookport silt loam, 107 in Leetonia stony loam, and 73 in Dekalb stony silt loam (steep phase). Other minor soil types accounted for 21 tenth-acre plots.

In computing the variation in forest growth on the major soil types of this virgin forest, the density of stocking, recorded in terms of the basal area in square feet measured at breast height for all trees 3.6 or more inches d.b.h., was used as a measure of the differences within samples of tenth-acre plots, and between the plot samples on these soils. (Sufficient total height measurements of the various tree species were not available to compare heights at maturity, sometimes used as a measure of site quality.)

Not only the basal area of all trees having minimum measurements of 3.6 inches d.b.h. and 70 feet total height, but further breakdowns of the data were compared for the three major soil types as follows: (a) the basal area of all hem-lock 3.6 or more inches d.b.h., hemlock 10 or more inches d.b.h., and hemlock 70 or more feet in total height; (b) the same items for beech, sugar maple, yel-low birch, and black cherry; (c) the number of stems per tenth acre by average diameter for all species; and (d) the total numbers of seedlings and saplings between 3.5 inches d.b.h. and 1 foot tall per hundredth-acre plot.

<center>RESULTS</center>

An analysis of the compositional differences found on the sample plots in the three major soil types gave essentially the same results as the study by Hough in which various topographic subdivisions were used. Table 1 indicates that the climatic climax hemlock-beech forest on the sample of 39.3 acres studied was rather uniform in tree species, regardless of soil type differences.

Further statistical tests were made of the variation between plots, using the actual square feet of basal area to indicate the stocking or productivity of the virgin forest on the three major forest types. No significant differences were found in the basal area of all living trees 3.6 or more inches in diameter, between any two of the three soil types compared. No significant differences in the basal area of trees in the dominant height class could be found for these soil types. The same is true for data on the number of stems per plot by average diameter

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[10] The classification used in mapping the soils on this tract is the one worked out during the last 40 years by the Bureau of Chemistry and Soils, of the U. S. Department of Agri-culture. The field work on soil type mapping was not influenced by reference to the previous work on the forest vegetation, and, naturally, the ecological strip cruise of 1930 was not affected by any preconceived ideas with regard to the influence of soil types on the forest growth.

for all species. Reproduction and sapling sizes did not differ significantly between any two of the major soil types[11].

The analysis of these samples to determine the differences in abundance of the individual tree species between various soil types shows that beech was significantly greater in square feet of total basal area, for all trees 3.6 or more inches d.b.h., on both the Cookport and the Leetonia than on the Dekalb soil[12]. The basal area of beech 70 or more feet in total height is also significantly greater on Cookport silt loam than on Dekalb stony silt loam. The basal areas of hemlock and of other major tree species in these size groups (including sugar maple) did not differ significantly between any two of the three major soil types. With regard to reproduction sizes (trees 1 foot tall to 3.5 inches d.b.h.) on the hundredth-acre samples, hemlock was significantly more abundant on the steep and

TABLE 1

Mean percentage of total basal area per tenth-acre plot in the East Tionesta virgin forest

SPECIES	SOIL TYPE			
	Leetonia	Cookport	Dekalb	Average*
	per cent	*per cent*	*per cent*	*per cent*
Hemlock	56.7	52.1	58.1	54.6
Beech	25.0	37.8	28.9	32.4
Sugar maple	3.6	3.6	6.2	4.1
Yellow birch	1.1	0.8	2.2	1.2
Others	13.6	5.7	4.6	7.7
All species	100.0	100.0	100.0	

Differences of 7.3 per cent are significant at the 1 per cent level.

* Based on 39.3 acres of sample plots subdivided into 393 strip plots of one-tenth acre each. This represents a cruise of about 5 per cent in an area of 934 acres of virgin forest.

rocky, north-facing Dekalb stony silt loam than on either the Leetonia or Cookport soils of the plateau upland (beech upland). Beech reproduction was also significantly more abundant on the Dekalb than on the Cookport soil and nearly reached a significant difference between the Dekalb and Leetonia soils. Evidently, reproduction conditions for all species are similar on the upland Cookport and Leetonia soils but favor hemlock and to a less extent beech on the north-facing slopes of Dekalb stony silt loam, possibly because of greater moisture from seepage and springs during critical seasons for seedling establishment.

[11] The results on two minor soil types, Dekalb silt loam and a poorly drained phase of the Dekalb, though based on much smaller samples, agreed in general with the results obtained on the major soil types.

[12] This is true despite the fact that beech on the Leetonia soil represents only 25 per cent of the total basal area of all species (table 1). It still outranks the actual basal area of beech on Dekalb stony silt loam, though lower in percentage with relation to other tree species.

DISCUSSION AND CONCLUSIONS

The evidence indicates, first, that the three major soil types found in the part of the East Tionesta virgin forest mapped in 1932 were distinctly different in profile characteristics. These differences have doubtless been created over a long period, primarily by differences in mode of formation (residual versus colluvial); in topographic location, which influences degree of slope and drainage or water table conditions; and in kind of parent rock material. Both parent material and topography affect the soil textural characteristics, especially the amount of rock fragments and the proportion of clay and silt present. The general climate, the physical aspect, and even the vegetative cover have presumably been fairly uniform for many years within this 934-acre tract of virgin forest. This is indicated by the presence of hemlock over 500 years old, by the absence of recent widespread windthrow evidence, and by the failure to find charcoal from past forest fires in the soil.

Secondly, it is apparent, from the analysis of sample tallies of virgin forest cover within each soil type, that no outstanding differences in the character of this forest could be found, regardless of the soil profile differences recognized.

The native forest tree species in this East Tionesta valley were evidently able to grow successfully on a fairly wide variety of topographic habitats and on different soil types. We may thus expect that in a given tract of old-growth timber, a variety of different and readily distinguishable soil types may exist without greatly influencing the kind or amount of tree growth present. Roe's study indicated that soil moisture relationships are probably the chief factor limiting the occurrence, degree of stocking, or growth of forest tree species on forest soils in the Lake States. In the local area studied in Pennsylvania, however, it is likely that soil moisture relationships did not differ sufficiently to affect tree growth even though profile differences had been created over a long period.

This forest is situated in a climatic region with ample and well-distributed rainfall, where virtually all soil types possess sufficient of the colloidal or silt fractions in the lower, if not in the top, layers to ensure adequate water-holding capacity during normal seasons. Major textural or other soil differences affecting water-holding capacity would become of critical importance, as limiting factors to tree growth, only during periods of extreme drought in such a region.

Detailed ecological studies by the Allegheny Forest Experiment Station on selected sample plots in the East Tionesta drainage area in 1934 show that climatic factors, such as periodic droughts and forest fires, wind and glaze storms, and biologic factors such as insects and disease, longevity, and competitive or reproductive ability of tree species, are fully as important as differences in soil types in influencing the character of the present-day virgin forest.

SUMMARY

Independent studies were made of soil types, based on profile characteristics, and of the species composition, abundance, and frequency of occurrence of trees in a virgin hemlock-beech forest in northwestern Pennsylvania.

The three major soil types in this forest differed in profile characteristics as a result of past geological, physiographic, and pedological history, especially drainage conditions.

Statistical comparisons of plots on each soil type, using basal area as an indication of productive capacity or stocking in this uneven-aged virgin forest, failed to reveal major differences in the average basal area or percentage species composition between any two of these three major soil types.

This is explained on the basis of (a) the adaptability of the native old-growth tree species to a rather wide variety of different sites, (b) the generally heavy texture of the Allegheny Plateau soils and abundant well-distributed precipitation, which tends to reduce the importance of soil factors as limiting to virgin tree growth, and (c) the action of certain powerful climatic and biotic factors, which are fully as important in guiding the development of the virgin forest as is the influence of existing soil type differences.
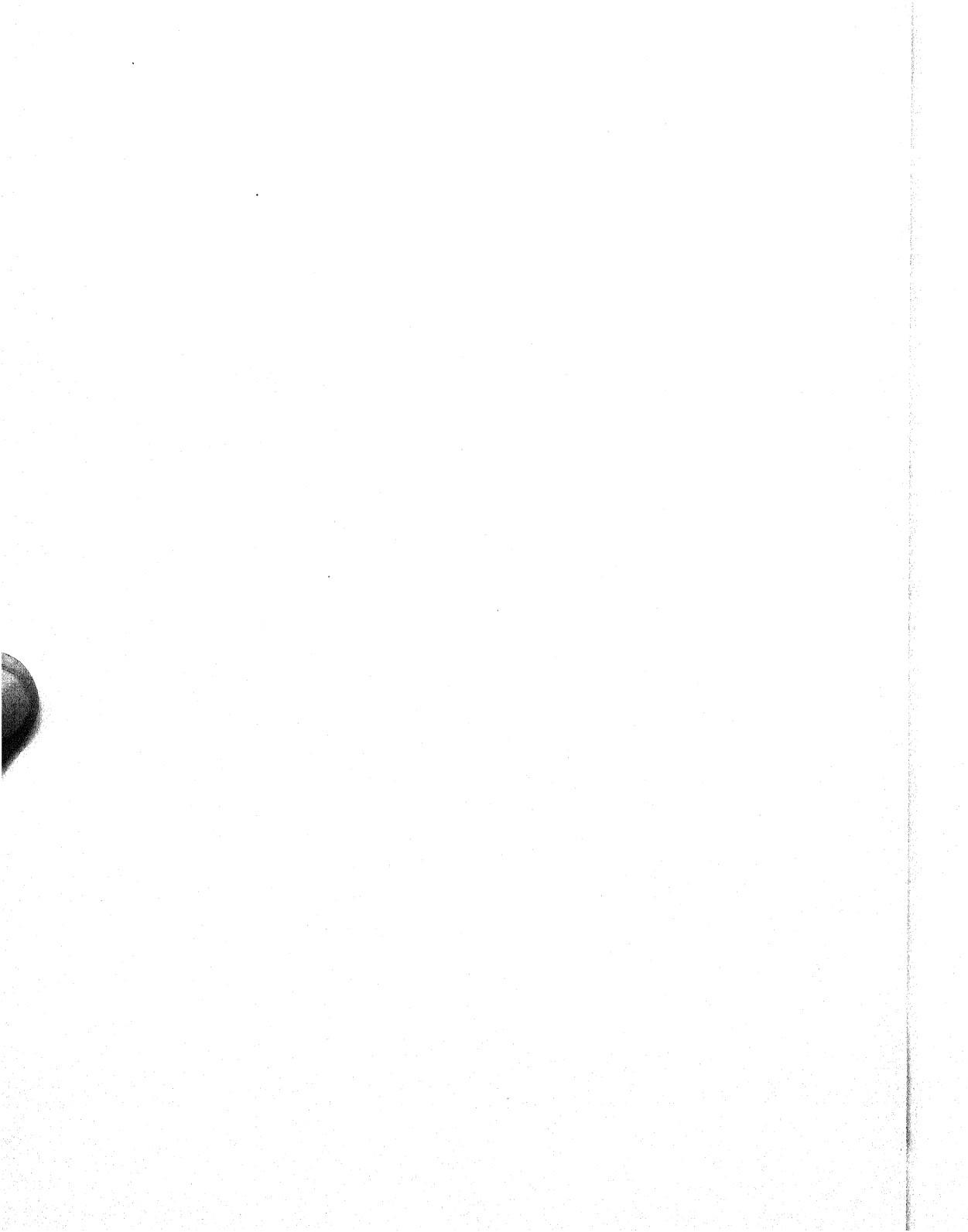
SOME CHEMICAL PROPERTIES OF SOIL ORGANIC MATTER AND OF SESQUIOXIDES ASSOCIATED WITH AGGREGATION IN SOILS[1]

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Many of the factors influencing aggregation in soils have received considerable attention. Little is known, however, about the chemical properties associated with different degrees of aggregation. By proximate chemical analyses of the organic matter in well-aggregated and in poorly aggregated fractions from each of several soils it was hoped that differences in the quality of the organic matter might help to explain some of the factors associated with aggregation in soils. The amount of sesquioxide extracted from the differently aggregated fractions by acid treatments was also investigated.

Metzger and Hide (7) found that the well-aggregated fraction of soil had a higher percentage of carbon and nitrogen than did the poorly aggregated fraction. Metzger (8) presented data on the effects of alfalfa on the carbon and nitrogen content of the soil. Waksman and Hutchings (13) have shown variations in the organic matter of different soil types. Gillam (5), however, points out that the humic acids from three widely different soil types are similar in the physical and chemical properties studied. The relation of free iron in the soil to aggregation has been pointed out by Lutz (6).

MATERIALS AND METHODS

Samples from eight soils from various locations in Kansas were selected for this study. Pertinent data with regard to these samples are presented in table 1.

Samples 5, 6, 7, and 8 are from the soil fertility series on the Kansas Agricultural Experiment Station Agronomy Farm and consist of a composite of 12 different locations from each plot. These samples were taken after the soils had grown alfalfa for 4 years in a 16-year rotation consisting of 4 years of alfalfa and 12 years of a minor rotation during which 1 year of corn was followed by 2 years of wheat. Surface soil taken to a depth of approximately 6 inches was brought into the laboratory, the clods were gently broken, and the samples were allowed to air-dry. Fifty-gram portions of the air-dry sample were placed in beakers, and the soil was covered with distilled water and allowed to stand 3 hours. At the end of this time the soil was washed into a cylinder $3\frac{1}{2}$ inches in diameter and having a volume of 1650 ml. The cylinder was completely filled with water, stoppered, and inverted 10 times. The suspension was allowed to settle for 30 seconds, and the upper 1000 ml. was then siphoned off rapidly. The soil con-

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tained in the suspension was considered as the poorly aggregated fraction. The remaining sediment was washed over a 24-mesh sieve. The material held on the sieve was designated the well-aggregated fraction.

Samples 1, 2, 3, and 4 were taken from a single location in each of four "slick spots," similar to that described by Ahi and Metzger (1). These samples were treated like the normal soils except that the well-aggregated fraction was collected on a 40-mesh instead of a 24-mesh sieve. This modification of procedure was necessitated by the fact that the material deflocculated to such a high degree in water that very few aggregates remained. These aggregates were concretionary in nature, had a rusty to dull black color, and resembled battered shot. They are probably similar to those described by Drosdoff and Nikiforoff (4) from Dayton silt loam.

TABLE 1

Type, origin, and cultural condition of soils from "slick spots" and from treated plots

SAMPLE NUMBER	SOIL TYPE	ORIGIN	CULTURAL CONDITION	LOCATION AND TREATMENT
1	"Slick spot"	Loessial	Cultivated	Kansas State College Agronomy Farm
2	"Slick spot"	Loessial	Cultivated	Kansas State College Agronomy Farm
3	"Slick spot"	Loessial	Virgin	Kansas State College Animal Husbandry Farm
4	"Slick spot"	Loessial	Virgin	Five miles north of Manhattan, Kansas
5	Geary silt loam	Loessial	Cultivated	Series I, plot 11, alfalfa untreated
6	Geary silt loam	Loessial	Cultivated	Series I, plot 12, brome grass plus manure*
7	Geary silt loam	Loessial	Cultivated	Series I, plot 9, alfalfa plus manure*
8	Geary silt loam	Loessial	Cultivated	Series I, plot 10, alfalfa plus manure and lime†

* Manure applied at the rate of 5 tons every third year from 1910 to 1940.
† 1500 pounds $Ca(OH)_2$ applied in July, 1937.

After separation, the materials were dried and ground to pass through a 100-mesh sieve, and determinations were made for total nitrogen and organic carbon as well as proximate chemical analyses of the organic matter. The amount of sesquioxides extracted in the acid treatments used in these analyses was also determined.

The total nitrogen determinations were made according to the Gunning-Hibbard method, and the organic carbon was determined by the Schollenberger method as outlined by Allison (2). The proximate chemical analyses were carried out by a modification of the method of Waksman and Stevens (12) as outlined by Shewan (10). The total organic matter was calculated by multiplying the percentage carbon by the factor 1.724.

EXPERIMENTAL RESULTS

Organic carbon before and after treatment

The percentage organic carbon in the original separates and after the various extractions is recorded in table 2.

In agreement with the findings of other workers, the percentage carbon was higher in all samples in the well-aggregated fraction than in the corresponding poorly aggregated fraction. With the exception of sample 1, the ratios of the carbon content of the poorly aggregated and the well-aggregated materials at the beginning of the study were similar to those existing at the end of the study. This indicates a similarity of carbonaceous materials extracted.

In the "slick spots," fairly low percentages of carbon were present in the poorly aggregated fractions as compared to those in the well-aggregated fractions. Since only a very small portion of this soil was aggregated, a low organic

TABLE 2

Organic carbon content of well-aggregated and poorly aggregated fractions before and after various extractions

SAMPLE	ORIGINAL FRACTION			PERCENTAGE INCREASE OVER SAMPLE 5		AFTER EXTRACTION			PERCENTAGE INCREASE OVER SAMPLE 5	
	A_1*	P_1	P_1/A	A_2	P_2	A_3	P_3	P_3/A_3	A_4	P_4
			per cent					*per cent*		
1	2.13	0.98	46.0			1.42	0.46	32.3		
2	3.60	1.18	32.7			2.31	0.77	33.3		
3	2.28	1.30	57.0			1.30	0.76	58.4		
4	2.85	0.87	30.5			1.81	0.56	30.9		
Ave.........	2.71	1.08	39.8†			1.71	0.64	37.4†		
5	2.32	1.37	59.0			1.35	0.77	57.0		
6‡	3.63	2.37	65.2	56.4	72.9	2.26	1.36	60.1	67.4	76.6
7‡	5.13	1.65	32.1	121.1	20.4	3.27	1.14	34.8	142.2	48.1
8‡	3.40	1.56	45.6	46.5	13.8	2.17	0.92	42.3	60.7	19.5
Ave.........	3.62	1.74	48.0†			2.26	1.05	47.5†		

* For convenience, A is used to indicate the well-aggregated fraction and is subnumbered progressively for each appearance in the table; P indicates the poorly aggregated fraction and is similarly subnumbered.

† Ratio of the averages of the data indicated at the head of the column.

‡ For rates of treatment see footnotes to table 1.

matter content for the soil is indicated. Sokoloff (11) concluded that sodium, either adsorbed or present in the soil solution, tends to promote depletion of the organic reserves of the soil.

Carbon changes in the fertility series

The percentage carbon changes occurring in the soil fertility series as a result of various treatments are likewise reported in table 2.

In the well-aggregated fractions the carbon content of the variously treated plots was much higher than that of the check. Although the brome grass plot, sample 6, showed considerable increase in the carbon content of the poorly aggregated fraction, there was only a small increase in this fraction in plots 7 and 8. Thus in both treated alfalfa plots, the increase in carbon occurred primarily in

the well-aggregated fraction. Peevy, Smith, and Brown (9) reported that the addition of lime speeded up bacterial action and that organic matter decomposed more rapidly. This would explain the considerably lower percentage of carbon in sample 8 than in sample 7. After the various extractions, the carbon content of the treated plots when compared with the check was higher on a percentage basis than before extraction. This indicates that the organic matter in the treated plots was more resistant to chemical decomposition than that in the check plot.

Analyses of organic matter in differently aggregated fractions

Samples 1–4 of table 3 give the proximate chemical analyses of the organic matter in both fractions of the "slick spots." In these samples both the ether-soluble and the alcohol-soluble materials were higher in the poorly aggregated than in the well-aggregated fraction.

Although the virgin samples, 3 and 4, were collected some distance from the cultivated samples, 1 and 2, and comparisons are not very reliable, some of the trends will be pointed out. The cultivated samples, 1 and 2, were virtually free of hemicellulose. Samples 3 and 4 both had a higher percentage hemicellulose in the poorly aggregated than in the well-aggregated fraction. In the cultivated samples the well-aggregated fractions contained the larger percentage cellulose, whereas in the virgin samples the poorly aggregated fractions were distinctly higher in cellulose. The data indicate that cultivation reverses the fraction in which the greater percentage cellulose is found. Although lignin and protein separates are larger than any of the other separates studied, no outstanding difference exists in the amount present in the differently aggregated materials.

The proximate chemical analyses of the organic matter in both fractions of samples 5–8 from the soil fertility series are also presented in table 3. In contrast to the data for the "slick spots," the ether-soluble materials are higher in the well-aggregated than in the poorly aggregated fractions. The percentages of alcohol-soluble materials, however, are higher in the poorly aggregated than in the well-aggregated fractions. These data agree with those for the "slick spots." On an average, the cellulose content is slightly higher in both fractions than the hemicellulose content. Although these soils are on the western edge of the prairie soils the data are in general agreement with Waksman and Hutchings' (13) results on chernozem soils from Texas and Oklahoma. The average percentage lignin is higher in the well-aggregated than in the poorly aggregated fraction. Various crop and fertilizer treatments on the soils represented by samples 6, 7, and 8 resulted in a lower percentage of ether- and alcohol-soluble materials in both fractions, in comparison with the untreated plot, sample 5. The treatments similarly raised the percentage of lignin but lowered the percentage of protein in both fractions. In the lignin separate this trend is slightly more pronounced in the well-aggregated than in the poorly aggregated fraction, whereas in the protein separate, the trend is stronger in the poorly aggregated fraction. These findings are in agreement with those of Waksman and Hutchings (13) on New Jersey treated plots.

On a percentage basis about one third of the organic matter is in the form of protein nitrogen remaining after the treatments. In the soil fertility samples the treatments decreased slightly the percentage protein nitrogen over that in the untreated plot. This difference was more apparent in the poorly aggregated fraction.

TABLE 3

Proximate chemical analyses of organic matter in well-aggregated and in poorly aggregated fractions

Analyses on a percentage basis

SAMPLE	CHEMICAL CONSTITUENTS													
	Ether-soluble material		Alcohol-soluble material		Hemicel-luloses		Celluloses		Lignins		Proteins		Sum of constituents accounted for	
	A*	P	A	P	A	P	A	P	A	P	A	P	A	P
"Slick spots"														
1	5.49	6.08	1.70	3.72	0.94	0.0	3.54	2.98	50.40	37.81	33.16	21.00	95.23	71.59
2	3.68	5.47	2.54	3.16	0.00	0.0	5.56	3.76	52.39	52.94	28.51	33.54	92.68	98.87
3	2.46	5.43	1.12	2.47	2.51	3.93	1.09	3.14	37.54	40.79	28.81	31.39	73.52	87.13
4	5.95	6.65	2.81	4.77	2.64	3.64	3.46	6.71	46.36	51.18	29.66	27.91	90.88	100.86
Ave......	4.39	5.91	2.04	3.53	1.52	1.89	3.41	4.51	46.67	45.68	30.04	28.46	88.07	89.62
Normal soils from fertility series														
5	3.96	1.90	2.06	2.53	3.69	2.02	5.47	1.79	44.05	43.65	28.84	31.63	88.07	83.52
6	2.16	0.68	1.51	1.91	1.74	2.10	4.35	0.32	51.20	45.20	26.82	27.60	87.78	77.81
7	1.43	0.55	1.76	2.02	1.51	0.0	2.60	0.95	53.17	53.22	28.08	25.22	88.55	81.96
8	1.52	1.46	1.84	2.06	2.01	0.0	0.67	5.15	50.41	45.19	28.60	28.60	85.05	82.46
Ave......	2.27	1.15	1.79	2.13	2.24	1.03	3.27	2.05	49.71	46.82	28.08	28.26	87.36	81.44

* See footnote *, table 2.

Total nitrogen

In table 4 are presented nitrogen data on the original fractions and on the fractions after treatment. The "slick spot" samples tended to have a wide ratio between the total nitrogen found in the two fractions, in comparison with the fertility series. In the "slick spots" and in sample 5, a slightly higher percentage of the nitrogen was extracted from the poorly aggregated fractions than from the well-aggregated fractions. This would indicate that the nitrogenous complexes are more stable in the well-aggregated fractions. In samples 6, 7, and 8 the nitrogen added by the various treatments was more easily released from the well-aggregated fractions than from the poorly aggregated ones. Treatments on samples 6, 7, and 8 raised the nitrogen content of the well-aggregated fractions considerably above the check plot. A much smaller percentage increase occurred in the poorly aggregated fractions with the exception of the brome and manure plot, represented by sample 6. Thus, the nitrogen added to plots 7 and

8 as a result of manure and lime treatments went primarily into the well-aggregated fraction. Lime along with manure tended to decrease the percentage nitrogen in sample 8 below that found in sample 7, which received only manure.

HCl-extracted nitrogen

That the amount of nitrogen extracted from the differently aggregated fractions of the soils was highly variable is evident from table 5. With one exception, a greater percentage of the total nitrogen was extracted from the poorly aggregated fraction with a 2 per cent HCl solution than from the well-aggregated fraction. This trend was very marked in the "slick spots," with the one ex-

TABLE 4

Nitrogen content of well-aggregated and poorly aggregated fractions before and after various extractions

As percentage of original fraction

SAMPLE	ORIGINAL FRACTION			AFTER EXTRACTION		
	A_1*	P_1	P_1/A_1	A_2	P_2	P_2/A_2
			per cent			*per cent*
1	0.1958	0.0572	29.2	0.0960	0.0241	25.1
2	0.2842	0.1095	38.5	0.1174	0.0402	34.2
3	0.1821	0.1130	62.0	0.1066	0.0631	57.2
4	0.2345	0.0670	28.6	0.1355	0.0363	26.7
Ave.........	0.2241	0.0867	38.68†	0.1139	0.0411	36.1†
5	0.1916	0.1200	62.6	0.0900	0.0490	54.4
6	0.2700	0.1810	67.0	0.1105	0.0805	72.8
7	0.3975	0.1310	32.9	0.1515	0.0725	47.8
8	0.2778	0.1240	44.6	0.1260	0.0590	46.8
Ave.........	0.2842	0.1390	49.9†	0.1195	0.0652	54.5†

* See footnote *, table 2.
† See footnote †, table 2.

ception, and also in sample 5. Approximately one fifth to two fifths of the total nitrogen in the well-aggregated fraction was released by this treatment; in the poorly aggregated fraction the figures are considerably higher.

The amide nitrogen extracted by the HCl treatment also varied widely. With but one exception, however, it was higher in the poorly aggregated fraction than in the well-aggregated fraction, on a percentage basis.

H_2SO_4-extracted nitrogen

In table 5 is also recorded the effect of the H_2SO_4 extraction on the soil nitrogen. The amounts extracted were less variable than those extracted with the HCl. The average percentage extracted from the "slick spots" was virtually

the same in both fractions. In the soil fertility samples, although the average percentage removed was slightly higher in the well-aggregated fraction, the individual results are too variable to warrant any definite conclusions. As was

TABLE 5

Total and amide nitrogen extracted from soil samples by acids

As percentage of original soil

SAMPLE	TOTAL NITROGEN IN HCl HYDROLYZATE					AMIDE NITROGEN IN HCl HYDROLYZATE				
	A_3*	P_3	P_3/A_3	A_3/A_1	P_3/P_1	A_4	P_4	P_4/A_4	A_4/A_1	P_4/P_1
			per cent	per cent	per cent			per cent	per cent	per cent
1	0.0473	0.0321	67.8	24.1	56.1	0.0244	0.0107	43.8	12.4	18.7
2	0.1128	0.0365	32.3	39.6	33.3	0.0398	0.0132	33.1	14.0	12.0
3	0.0333	0.0338	101.5	18.2	29.9	0.0116	0.0127	109.4	6.3	11.2
4	0.0487	0.0199	40.8	20.7	29.7	0.0237	0.0082	34.5	10.1	12.2
Ave.........	0.0605	0.0306	50.5†	26.9†	35.3†	0.0249	0.0112	44.9†	11.1†	12.9†
5	0.0754	0.0655	86.8	39.3	54.5	0.0272	0.0237	87.1	14.1	19.7
6	0.1021	0.0762	74.6	37.8	42.0	0.0376	0.0283	75.2	13.9	15.7
7	0.1566	0.0566	36.1	39.3	43.2	0.0520	0.0215	41.3	13.0	16.4
8	0.1174	0.0568	48.3	42.2	45.8	0.0461	0.0244	52.9	16.5	19.6
Ave.........	0.1129	0.0638	56.5†	39.7†	45.8†	0.0407	0.0245	60.1†	14.3†	17.6†

SAMPLE	TOTAL NITROGEN IN H2SO4 HYDROLYZATE					AMIDE NITROGEN IN H2SO4 HYDROLYZATE				
	A_5	P_5	P_5/A_5	A_5/A_1	P_5/P_1	A_6	P_6	P_6/A_6	A_6/A_1	P_6/P_1
			per cent	per cent	per cent			per cent	per cent	per cent
1	0.0746	0.0227	30.4	38.1	39.6	....	....	....	....	....
2	0.0939	0.0304	32.3	33.0	27.7	....	....	....	....	....
3	0.0435	0.0302	69.4	23.8	26.7	0.0118	0.0110	93.2	6.4	9.7
4	0.0669	....	....	28.5	....	0.0158	0.0056	35.4	6.7	8.3
Ave.........	0.0697	0.0278	39.8†	31.1†	32.0†	0.0138	0.0083	60.1†	6.1†	9.5†
5	0.0504	0.0288	57.1	26.3	24.0	0.0114	0.0008	85.9	5.9	8.1
6	0.0740	0.0495	66.8	27.4	27.3	0.0158	0.0141	89.2	5.8	7.7
7	0.1189	0.0413	34.7	29.9	31.5	0.0228	0.0070	30.7	5.7	5.3
8	0.0780	0.0280	35.8	28.8	22.5	0.0163	0.0095	58.2	5.8	7.6
Ave.........	0.0804	0.0369	45.8†	28.6†	26.5†	0.0166	0.0101	60.8†	5.8†	7.2†

* To facilitate comparisons between the nitrogen tables, the subnumbers increase progressively through tables 4 and 5.

† See footnote †, table 2.

true in the HCl hydrolyzate, the amount of amide nitrogen extracted from the different samples varied widely but was relatively higher in the poorly aggregated fractions than in the well-aggregated fractions in all but one of the soils.

Nitrogen and carbon in various sized aggregates

In the fertility samples, 5–8, additional separations were made on the basis of aggregate size. The percentage nitrogen and carbon decreased with decreased particle size, with the exception of the colloidal fraction, which was high in both. The greatest decrease occurred between the fraction held on a 60-mesh sieve and that passing through it and settling in 30 minutes. These data are in general agreement with Metzger and Hide's (7) results except that the differences between the various sized particles were sharper because of cleaner separations.

Sesquioxides precipitated from the acid hydrolyzates

In table 6 are presented data on the amounts of sesquioxides precipitated from the HCl and the H_2SO_4 hydrolyzates.

TABLE 6

Sesquioxides extracted from soil samples by acids

As percentage of original soil

SAMPLE	HCl HYDROLYZATE			H_2SO_4 HYDROLYZATE		
	A*	P	P/A	A	P	P/A
	per cent	per cent	per cent	per cent	per cent	per cent
1	8.51	2.27	26.6	8.83	2.16	24.4
2	9.30	1.77	19.0	4.62	1.27	27.4
3	2.64	2.13	80.3	3.63	2.34	64.4
4	7.27	2.30	31.6	6.20	1.77	28.5
Ave.........	6.93	2.12	30.6†	5.82	1.88	32.3†
5	3.40	2.93	86.1	2.45	1.64	66.9
6	3.62	3.17	87.5	2.34	1.97	84.1
7	4.26	2.89	67.8	2.20	2.29	104.0
8	3.89	3.00	77.1	2.37	1.65	69.6
Ave.........	3.79	3.00	79.1†	2.44	1.89	77.4†

* A, well-aggregated fraction; P, poorly aggregated fraction.

† See footnote†, table 2.

Since in all cases the amount of sesquioxides extracted from the well-aggregated fractions was considerably greater than that extracted from the poorly aggregated fraction, the probability that in the prairie soils sesquioxides act as a cementing agent should not be overlooked. Lutz (6) has shown that in the lateritic soils of the Southeast the proportion of aggregates is roughly proportional to the amount of readily soluble iron. In the samples from the soil fertility plots, the higher degree of aggregation was associated with an increase of approximately 20 per cent in readily extractable sesquioxides.

The limited number of aggregates which were found in the "slick spot" soils were high in sesquioxides in comparison with the poorly aggregated soil, which,

with the exception of sample 3, yielded only about one fourth as much sesqui-oxides as the well-aggregated fraction. Although the "slick spots" are relatively unimportant agriculturally, the interesting feature about these soils is that although only a few aggregates are formed, these appear to be formed principally by the iron present and not by the organic matter. Baver and Hall (3) found that a sodium humate may be dehydrated, but the reaction is reversible, and when the humate is again wetted it is subject to further loss by leaching. Thus the influence of organic matter on aggregation in a "slick spot" is negligible. In the normal soils, samples 5–8, the hydrogen and calcium humates are virtually irreversible once they have been dehydrated; thus the organic matter assumes greater importance in aggregate formation in normal soils. The binding effect of the iron is evidently of importance, however, as shown by the increased amounts present in the well-aggregated fractions.

SUMMARY AND CONCLUSIONS

Proximate chemical analyses of the organic matter and related data were obtained for a well-aggregated and a poorly aggregated fraction of eight Kansas soils. These represent four "slick spots" and four differently treated plots of the fertility series of the Kansas Agricultural Experiment Station Agronomy Farm.

Cultivation and various soil treatments changed the chemical composition of the organic matter of some of the fractions. The carbon and nitrogen content was distinctly higher in the well-aggregated than in the poorly aggregated fractions.

The alcohol-soluble portion of the organic matter was relatively low in the well-aggregated fraction in all cases. The ether-soluble material was also low in the well-aggregated fraction of the "slick spots," but in the fertility plots the reverse was true.

As a result of certain soil treatments the lignin content of the organic matter of both of the differently aggregated fractions of the soil fertility samples was increased, but the protein content was decreased.

In general the nitrogenous material in the poorly aggregated fraction was more completely extracted by hydrolysis with weak HCl than was that in the well-aggregated fraction. This was not true for the H_2SO_4 treatment. Both acid hydrolyzates of the poorly aggregated fractions tend to contain a relatively high proportion of their nitrogen in the amide form.

Larger amounts of sesquioxides were removed by the acid extractions from the well-aggregated fraction than from the poorly aggregated fractions. In the "slick spots" this difference averaged more than three to one.

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THE SOURCE AND PHOSPHATASE ACTIVITY OF EXOENZYME SYSTEMS OF CORN AND TOMATO ROOTS[1]

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While studying the availability of organic phosphorus to corn and tomato plants, Rogers, Pearson, and Pierre (30) discovered that the roots of these plants have a mineralizing action on the organically bound phosphorus in several carriers. Some of the compounds being tested were unstable in the presence of plant roots, undergoing hydrolytic decomposition and releasing inorganic phosphorus to the test solutions. Sufficient evidence was presented to show that the decomposition of these compounds was not microbial but was attributable to hydrolytic enzymes which are held in the sloughed-off cellular material coating the roots. Recognition of the importance of a mechanism by which plant roots are able to decompose complex organic substances led to further study of the source and activity of these exoenzyme systems. The investigations were developed along two lines: first, an examination was made of the root structure and the release of cellular materials during normal root growth; second, some of the major factors affecting the intensity of the phosphatase activity of corn roots, principally temperature and acidity, were investigated.

HISTORICAL

Root structure and the release of cellular materials and excretions from roots

It is recognized that true excretions of enzymes from the roots proper could have contributed to the rapid hydrolysis of some of the compounds that were observed in the previous studies (30). Such an assumption is not at all necessary, however, to explain the root action that was observed. No attempt will be made to review the vast literature on root excretions, but a few studies that appear especially pertinent will be mentioned.

Merrill (25) in 1915 gave a fairly comprehensive review of reports on root excretions up to that time. He pointed out that Link in 1848 first suggested that "the slimy drops held on root tips were not excretions but castoff root cap cells," and that Molisch in 1887 proposed that root excretions may exert an effect on organic substances in the soil and that this may be more important than their solvent action on inorganic materials. An "extracellular" oxidizing power of roots was demonstrated by Schreiner and Reed, who added various chromogens to solutions with roots present and observed color changes on the roots (33).

Lyon and Wilson (23) grew corn, oats, peas, and vetch in sterile nutrient solutions and studied the liberation of organic materials into the solutions and the deposition of sloughed-off cells in the bottom of the culture vessels. They reported that surprisingly large amounts of carbonaceous material were released from roots. In addition, they observed the presence of reducing substances and ammonia nitrogen in the solutions, although no ammonia nitrogen was supplied the plants. It was suggested that this ammonia could have resulted from enzymatic action of root-excreted catalysts on organic nitrogen, which was found in solution and in the cellular material in the flasks.

The developmental histology and structure of stems of the economic plants have been much more thoroughly studied than the roots of these plants. A release of root-cap and epidermal cells to the rhizosphere has, however, been long recognized by botanists (9, p. 93; 10, p. 43; 41, p. 37) as a normal process in root growth. Haberlandt (9, p. 94) described as one function of this coating of senescent cells lubrication of the growing point of the root as it forces its way through the soil. Generally this sloughing-off of the root cap has been assigned a protective role.

Various workers (7, 21, 32, 36, 37) have pointed out the attractiveness of roots and their immediate environment to microorganisms in the soil. Thom (37) attributed the increased microbial activity at the root surface to a continual release of epidermal and root-cap cells. Linford (22), on the other hand, contended that the concentration of microorganisms in the rhizosphere during the early stages of root growth was not dependent upon the destruction and utilization of senescent or dead root-cap cells, root hairs, and cortical tissue. Nevertheless, this concentration of microbial activity in the immediate environs of the root is strongly suggestive that the release of cellular material by normal roots may reach considerable proportions.

The nature and viability of the detached root-cap cells have received some attention. Chambers (3) cultured fragments of root tips of squash and observed a migration of individual cells on agar media, as well as a marked elongation of these cells after separation from the root tip. He also noted a viscid film diffusing from the fragments, although some of the released cells remained viable for 30 days. Knudson (14) refuted the commonly held belief that most root-cap cells are either dead or short-lived when lost from roots and reported that some detached root-cap cells maintained themselves for 71 days. Robbins, Bartley, and White (28) failed to observe cell migration of the type reported by Chambers (3) but observed an extrusion of protoplasm from some of the half-moon-shaped cells which were released from the root cap. Roberts (29) reported having seen epidermal cells (root hairs) burst when placed in solutions of lower osmotic pressure, eject part of their contents, and resume their original appearance through the wall membrane's springing back into place. Howe (11) found the content of the root-hair cells to be acid in reaction (pH 5.2 to 6.8).

Knudson and Smith (15) raised the question as to whether plants can feed in a manner similar to that of fungi, by means of enzyme excretions. Knudson claimed (16) to have demonstrated what he termed a "secretion" of invertase

from corn roots in sterile cultures, but failed to obtain evidence of a similar release of amylase (15). Furthermore, he questioned whether the invertase action that he had observed could have originated entirely in the small amount of cellular root-cap material that had been released. Apparently he ignored the residue of cells commonly found covering the roots and resisting displacement therefrom in aqueous solutions. Pryanishnikov (27) attributed the beneficial effect of lupines on cereals, when grown together, to the solvent action of root excretions from the lupines.

Occurrence and characteristics of some of the plant phosphatases

The distribution of phosphatases in various organs of plants has received very little attention. Their presence in certain tissue zones of the root becomes important in studying the enzymatic activity of sloughed-off cells. Ignatieff and Wasteneys (12), using powdered tissue, studied the distribution of glycerophosphatase in the various organs of several different plants. They found the phosphatase activity in young bean roots sufficient to release 5 mgm. of inorganic phosphorus per minute per gram of dry matter from 2 per cent sodium β-glycerophosphate at pH 5.8 and 37.5°C. This activity in the root decreased with increasing age of the plant and was present to a lesser degree in the roots of radish, potato, and wheat.

Phosphatases from animal sources have been much more extensively studied than those occurring in plants. The phosphomonoesterases, referred to as the "common" phosphatases (2, p. 505), are capable of splitting phosphoric acid from a large number of phosphate esters. Included in this list are the salts of glycerophosphoric acid.

Several investigators (2, p. 505; 6, p. 169; 18) regard nucleotidase, which is capable of hydrolyzing the mononucleotides, as a nonspecific phosphomonoesterase. On the other hand, polynucleotidase (20) is regarded as a specific enzyme for this substrate. Nucleic acid, being a polynucleotide (19, p. 274), apparently requires a specific enzyme (polynucleotidase) to separate its constituent mononucleotides before complete dephosphorylation of these structural units can be effected by the common phosphatases (mononucleotidase).

If the structure of yeast nucleic acid is assumed to be that proposed by Levene and Base (19, p. 250)—and the best evidence seems to support such a structure—it appears that the phosphoryl group of adenylic acid which is linked to only one ribose unit should be susceptible to hydrolysis by mononucleotidase without the previous action of an enzyme to separate the nucleotides. This is based on the assumption that space relationships or some other factor peculiar to the larger molecule would not interfere with the action of common phosphatases on the nucleic acid molecule. If such a reaction is possible, the common phosphatases would release one fourth of the phosphorus of nucleic acid without the preparatory action of polynucleotidase, which might explain some of the contradictory reports on the specificity of mononucleotidase.

MacFadyen (24) offered evidence that the route of decomposition of nucleic acid by *Bacillus subtilis* was in the following order: (a) separation of the four

mononucleotides, (b) separation of the phosphoric-acid–ribose ester from the nitrogenous bases, (c) chemical hydrolysis of the phosphoric-acid–ribose ester in slightly acid or neutral solutions.

Polynucleotidase is regarded by Gulland and Jackson (8) as a diesterase and as a specific enzyme for splitting the nucleotide polymers. The nonspecific enzyme, which is capable of dephosphorylating the mononucleotides and glycerophosphates, appears to be one of the most common phosphatases in animal and plant tissues.

In general, the plant phosphatases have maximum activity in acid media, whereas the phosphatases from animal sources have their optimum reaction in alkaline solutions.

Kay and Lee (13) studied the rates of hydrolysis of α- and β-isomers of glycerophosphate with taka and soybean phosphatases and reported different pH curves for the two isomers.

Plant enzymes in general appear somewhat more thermostable than the organic catalysts from animal sources. Temperature coefficients over the more favorable part of the range are of the order, $Q_{10} = 2$ to 3. Tauber (35, p. 3) asserted that most enzymes in solutions are inactivated at about 50°C. and that destruction is complete at 80°C. Van Slyke and Cullen (38), however, reported an optimum temperature for urease of 55°C. in 15-minute measurements.

EXPERIMENTAL MATERIALS AND METHODS

Microscopic examination was made of the gel-like accumulations on the larger root tips of corn plants grown in solution cultures. Smear slides of the disorganized cellular material, stained with acetocarmine, were prepared and studied at several different stages of growth of the roots.

Temperature and pH activity curves were obtained for glycerophosphatase and nuclease systems by suspending excised corn root tips in solutions containing organic phosphorus (approximately 100 p.p.m. PO_4) and determining the amount of inorganic phosphorus released after a period of incubation. The source and method of preparation of the stock solutions of the organic phosphorus compounds were as previously described (30). A few drops of toluene were added to each flask or test tube as an antiseptic, and adequate controls with the buffers or distilled water were included in each test. The general technique was to suspend four large corn roots in 20-cc. test tubes (fig. 1) which were nearly filled with the organic phosphorus solutions buffered to the desired pH. In the case of nucleic acid the ammoniacal solutions were buffered with ammonium tartrate and H_2SO_4, and preliminary tests were made to approximate the optimum pH for the nuclease system. In these preliminary tests the gelatinous cellular material (fig. 2) was collected from the corn root tips with a small pipette and suspended in sterile solutions of the organic compounds.

A supplementary investigation was made to determine whether the high temperatures employed in these tests were producing a release of enzymes from the roots to the test solutions. This involved preheating roots in the buffer solutions for 6 hours at temperatures from 27° to 70°C. The tubes were then removed

from the ovens, nucleic acid was added, and the tubes were kept at room temperature for 12 hours. As no difference was found between the phosphatase activity of the root suspensions that had been preheated at 60° or 70°C. and those kept at 27°C., it was concluded that these temperatures did not cause any abnormal excretion of enzyme from the roots.

In all of the tests with excised roots, care was taken to keep the cut ends of the roots out of the solutions. This was accomplished by suspending the roots from cotton plugs. The control samples served to check the effect of the buffers, toluene, and incubation treatment on the roots and also on the chemical stability of the test solutions.
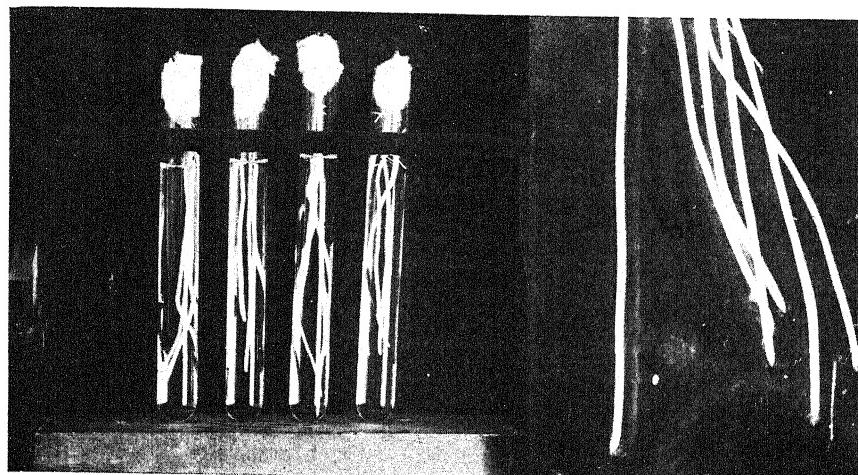
FIG. 1.   FIG. 2.

FIG. 1. EXCISED CORN ROOTS SUSPENDED IN TEST TUBES FOR A STUDY OF PHOSPHATASE ACTIVITY

FIG. 2. TUFTS OF CELLULAR MATERIAL ON THE TIPS OF ACTIVELY GROWING CORN ROOTS IN SOLUTION CULTURES

RESULTS

Sources of the "extraroot" enzymes

Having identified the enzymatic activity of corn roots with the gelatinous material coating the roots in solution cultures, the nature and the origin of this residue of root growth were investigated. Figure 3 is a photomicrograph[3] of some of the sloughed-off cells from young corn roots. In figure 4 a longisection of the root cap shows the cells in all stages of release. The cells appear in excellent condition and well nucleated, with little evidence of having undergone deterioration or having lost any of their contents. Similar preparations of the gelatinous material collected at later stages of growth of the plants showed some free nuclei and empty cell walls.

[3] The authors wish to acknowledge the cooperation of J. E. Sass, who assisted with the root structure studies and kindly prepared the photomicrographs, figures 3, 4, and 5.

In the process of detachment the individual cells appear to break loose at the ends first. These ends then curve outward away from the underlying tissue, and many of the cells assume a sickle shape after release from the root cap. There is evidence that considerable swelling and elongation of the single cells take place after release from the root, but as suggested by Knudson (14) and Chambers (3), many of the cells appear to remain intact and well nucleated for a considerable period. No attempt was made to measure the length of life of these cells or their behavior under the culture conditions employed in these studies, other than microscopic examination of their appearance at several stages of root growth.

Some idea of the relative size of the corn root cap in comparison with the dimensions of the other tissue zones of the root can be obtained from figure 5.
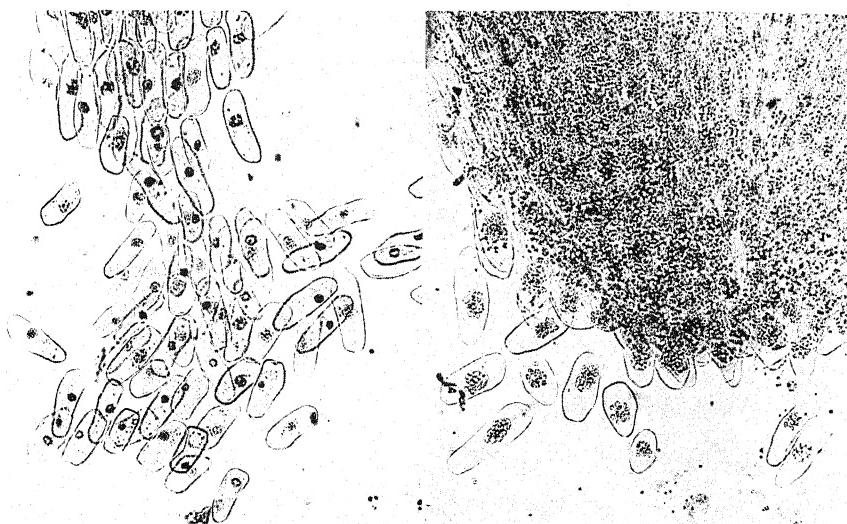
FIG. 3. SLOUGHED-OFF ROOT-CAP CELLS OF   FIG. 4. LONGISECTION OF ROOT CAP OF A
    CORN SOON AFTER RELEASE × 166   YOUNG PRIMARY ROOT OF CORN × 166

Sommer and Sorokin (34) reported that boron deficiency caused a severe stunting of root-cap development or prevented it entirely. Figure 6, a transection of a root tip (just above the root cap) of sorghum (4), shows a border of root-cap cells breaking away from the palisadelike epidermal cells. Other transections of the root-hair zone of corn roots revealed the sloughing off of the epidermis and one or more layers of hypodermal cells before lignification of an outer layer developed a permanent protective covering.

In dicotyledonous plants the periderm is initiated in the pericycle, and this corky layer eventually cuts off the cortex and epidermis from the vascular system. As a result of this periderm activity the cortical tissue and the epidermis are ruptured and released to the rhizosphere.

The mucilaginous nature of residues of microbial growth has been recently assigned a role in producing favorable tilth in soils (26). One explanation of

the beneficial effect of extensively rooted sod crops on soil aggregation may be the continual release of cellular material to serve both as a stimulant for microbial activity and possibly as a temporary cementing agent. Though quantitative measurement of the amounts of cellular material released to the rhizosphere during normal growth under field conditions appears difficult, histological evidence from several sources suggests that the amount must be considerable. The perennial monocotyledonous plants, which have been observed to be continually renewing their root system, and the dicotyledonous ones, which lose not only root-cap and epidermal tissue but all of the cortex as well, would appear to contribute especially large amounts of organic material to the rhizosphere during the normal growth of the plant.
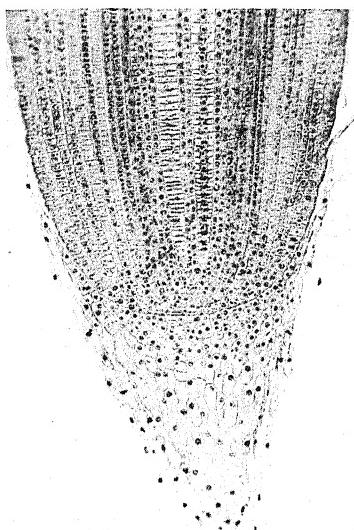
FIG. 5. LONGISECTION OF YOUNG CORN ROOT TIP, REVEALING RELATIVE SIZE OF ROOT CAP AND OTHER TISSUE ZONES × 75
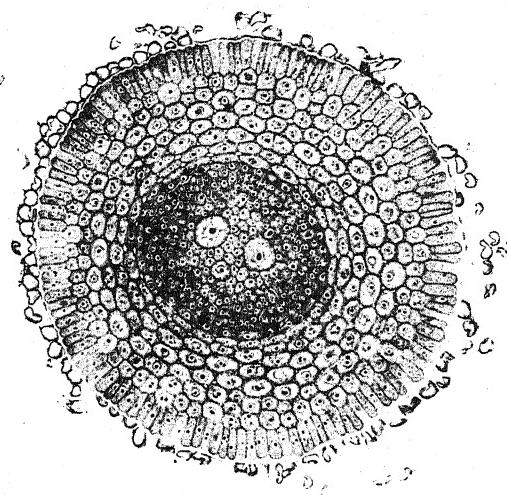
FIG. 6. TRANSECTION OF SORGHUM ROOT NEAR TIP, SHOWING DETACHMENT OF ROOT-CAP CELLS × 166 [AFTER CHI (4)]

Effect of previous level of phosphorus nutrition of the plant on phosphatase activity of the roots

Corn and tomato plants which had been grown on a minimum phosphorus supply were divided into two groups. One group of plants was kept in solutions with 5.0 p.p.m. inorganic phosphorus for 8 days, whereas the other group was deprived of phosphorus until the plants showed definite deficiency symptoms. The phosphorus-fed and the phosphorus-starved plants were then placed in solutions of calcium glycerophosphate and of nucleic acid for 6 hours, and the change in inorganic phosphorus concentration in the solutions was measured as an indication of the intensity of phosphatase activity. Nucleic acid underwent

some mineralization of its phosphorus, but no difference could be noted between the hydrolyzing action of phosphorus-fed and phosphorus-starved plants.

As shown in table 1, phosphorus-deficient corn and tomato plants showed slightly more glycerophosphatase activity than did the plants that had been given ample phosphorus. It is probable that the real differences in phosphatase activity are greater than the data indicate, since the phosphorus-starved plants were probably absorbing inorganic phosphorus faster than were the plants previously well supplied with the element.

TABLE 1

Amounts of phosphorus mineralized from calcium glycerophosphate (in excess of absorption) by corn and tomato roots of phosphorus-fed and phosphorus-starved plants

PLANT AND TREATMENT	PHOSPHORUS MINERALIZED FROM CALCIUM GLYCERO-PHOSPHATE IN EXCESS OF ABSORPTION
	p.p.m. PO₄
Corn grown on minimum phosphorus supply and given no phosphorus for 8 days prior to tests....................................	2.61
Corn grown same as above but a concentration of 5 p.p.m. inorganic phosphorus maintained in the solutions for 8 days prior to tests....	Difference 1.83
	0.78
Tomatoes grown on a minimum phosphorus supply and given no phosphorus for 3 weeks prior to tests............................	2.55
Tomatoes grown same as above but a concentration of 5 p.p.m. inorganic phosphorus maintained in the solutions for 8 days prior to tests...	2.40
	Difference 0.15

Effect of H-ion concentration and of temperature on the phosphatase activity of corn roots

Glycerophosphatase. A range in H-ion concentration from pH 2.0 to 8.0 was studied for the enzyme glycerophosphatase. The temperature was maintained at 27°C. for 12 hours. As shown by the data in figure 7, maximum activity occurred at pH 4.0, the rate falling off sharply above and below this point.

The temperature curve was obtained with solutions buffered to pH 4.0 and held for 9 hours at temperatures ranging from 20° to 70°C. The activity of the enzyme increased rapidly from 20° to its peak at 45° and decreased abruptly thereafter to about the same level at 60° as it showed at 20°. Boiling a suspension of the gel completely destroyed its glycerophosphatase activity.

The optimum reaction (pH 4.0) for glycerophosphatase of corn roots approaches the H-ion concentration reported by Kay and Lee (13) and by Kobayashi (17) for maximum taka-phosphatase activity. As previously mentioned, the former workers obtained slightly different optimum reactions for the α- and β-forms of glycerophosphate, as well as different optimums for soybean-phos-

phatase and the taka-enzyme on the same isomeric form of glycerophosphate. It is highly probable that the commercial preparation of calcium glycerophosphate used in these studies was a mixture of the two isomers.
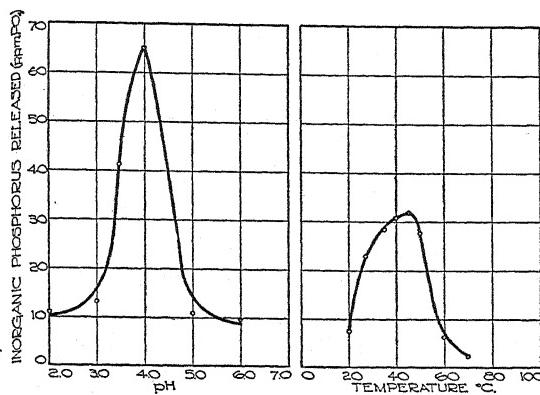
FIG. 7. EFFECTS OF pH AND TEMPERATURE ON DEPHOSPHORYLATION OF CALCIUM GLYCERO-PHOSPHATE BY CORN ROOTS

Initial concentration of organic phosphorus was 100 p.p.m. P. The pH curve was obtained from 12-hour incubations at 27°C.; temperature cruve from 9-hour incubations at pH 4.0.
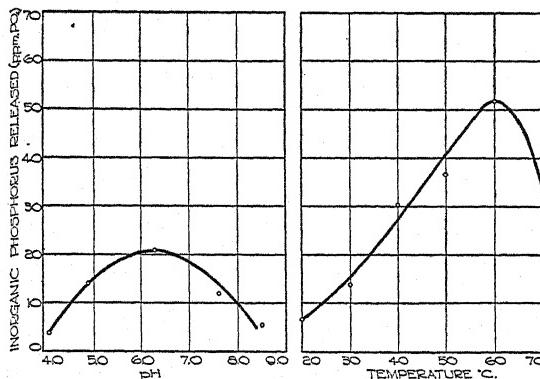
FIG. 8. EFFECTS OF pH AND TEMPERATURE ON DEPHOSPHORYLATION OF NUCLEIC ACID BY CORN ROOTS

Initial concentration of organic phosphorus was 100 p.p.m. P. The pH curve was obtained from 12-hour incubations at 27°C.; temperature curve from 12-hour incubations at approximately pH 7.0.

Nucleases. Because of the ease of chemical decomposition of nucleic acid, it was found necessary to take special precautions in the hydrolysis tests with this compound. Only fresh dilute solutions of the polynucleotide were used.

The effects of H-ion concentration and temperature on rate of dephosphorylation of nucleic acid are shown in figure 8. The activity curves for the nuclease

system were widely different from those for glycerophosphatase.   The pH curve for dephosphorylation of nucleic acid approaches a true parabola, with the optimum at about pH 6.3, less sharply defined than that for glycerophosphatase. Similar results were obtained in preliminary tests in which a water suspension of the gelatinous mass of sloughed-off cells from corn roots was added to sterile solutions of nucleic acid.   Maximum activity was obtained in these tests at pH 7.0, with 1.8 per cent mineralization at pH 4.6, 3.6 per cent at neutrality, and 2.4 per cent at pH 8.0.   The optimum temperature for the nuclease system, as measured by inorganic phosphorus release in 12 hours at approximately pH 7.0, was found to be about 60°C. where its activity was 44 per cent greater than at 45°, the optimum for glycerophosphatase.

Some difficulty was experienced in maintaining a constant pH of the nucleic acid solutions during the course of incubation in the temperature series.   As a result, the H-ion concentration of the samples which were held at 60°C. was somewhat greater (pH 6.3) than that for the rest of the samples in this series. As the nuclease system appeared resistant to slight changes in pH in the vicinity of optimum temperature, however, any effect of this slight increase in acidity is minimized.   Furthermore, other investigations (31) which dealt with the mineralization of the phosphorus in yeast nucleic acid by soil catalysts showed a maximum activity at the same temperature (60°C.) as was found optimum for the nuclease system of corn roots in this study.

The effects of H-ion concentration and temperature on the activity of root-borne phosphatases are in agreement with the observation that enzymes from plant sources are generally more tolerant to acidity and heat than are those from animal sources.   Bodansky (1) reported an optimum temperature for co-agulation of milk by a plant enzyme between 80° and 85°C. in 15-minute incubations, and Conrad (5) found some thermostable urea-hydrolyzing catalysts in soil.

No attempt was made to separate the responses of the two enzymes that are involved in the dephosphorylation of nucleic acid.   The activity of the enzyme needed to separate the nucleotides (polynucleotidase) appeared to be limiting the system in the preparations that were held at 27°C., since the maximum activity of the nuclease system in this series was much less than the activity of glycerophosphatase at the same temperature—assuming glycerophosphatase and mononucleotidase to be identical enzymes.   Obviously the curves shown in figure 8 for the nuclease system do not necessarily reflect optimum conditions for polynucleotidase activity, since these curves were based on release of inorganic phosphate.   Since the nuclease system and glycerophosphatase have different optimum reaction and temperature conditions, even though they have a common phosphatase, the difference in their activity curves may be attributed to different pH and temperature optimums for the two enzymatic reactions in the nuclease system.

DISCUSSION

In plant nutrition studies the more recent findings point to an advantage in having a close contact of the root with the source of the nutrients.   For the

mineralizing action of roots to be most effective in releasing available nutrients from slowly soluble organic materials a root-soil contact would be necessary.

The relative importance of such a relationship between the plant root and the soil mass in plant nutrient absorption under field conditions remains to be established. It appears, however, that the existence of a mechanism by which plants are enabled to digest certain organic forms may have far-reaching implications in practical soil fertility problems. For example, an interpretation of results from studies of soil extracts and displaced solutions by conventional methods would be exceedingly difficult if the solvent action of plant roots on the organic form of nutrients in soils is extensive. Evidently such a process necessarily complicates the problem of estimating the fertility needs of a highly complex soil-plant system. The role of the plant is emphasized and another explanation is offered for the inadequacy of chemical soil tests alone in estimating fertility needs.

Early recognition of this sloughing away of certain root tissues as a normal process during root growth led to little more than mere speculation as to what the role of such a process might be in the nutrition of the plant. The process was assigned, quite summarily it seems, the function of lubricating or protecting the advancing root tip as it forced its way into the soil.

Evidently the higher plants do possess an "extraroot" digestive system which originates in the cast-off root tissue. This might be likened to the extracellular digestive enzymes of the lower forms. Obviously the nature of this system will depend largely upon the contents of the root cells at the time they are divorced from the root proper and cease to exchange materials with the conductive tissue of the plant. Although these cells would be expected to be fairly rapidly attacked by microorganisms under normal field conditions, destruction of the cell walls would not be prerequisite to enzymatic activity by this gelatinous mass of cells.

It should be recognized, however, that such a release of readily available organic material, which begins early in the growth of the plant, would stimulate transformations involving the nutrient supply to the higher plants, through increased microbial activity in the immediate environs of the root. It appears that this release of root tissue may be either beneficial or detrimental to the nutrition of the parent plant, depending upon a number of factors. The nature of the soil population, the chemical composition and enzymatic properties of the material released by the plant, and the nature and amount of nutrients already present in the soil all will influence the net result on the immediately available nutrient supply.

The whole question of direct absorption of organic nitrogen could well be reviewed in the light of such evidence of exoenzyme systems of plant roots. Plant association studies involving legume and nonlegume plants may be subject to new interpretations if excretion of organic forms of nutrients from legume nodules is extensive and nonlegume roots carry the mechanism for mineralizing the materials released in organic form. Obviously, Virtanen's (39) explanation of his observation that the nitrogen produced by nodules on red clover was indispensable for optimal growth of the legume must be questioned. He claimed

that 77 per cent of the nitrogen excreted from legume nodules was in the form of nucleic acid and explained the superiority of organic nitrogen from the nodules over NH_4NO_3 as due to direct absorption and assimilation of the former in the synthesis of proteins within the plant. Later (40) he reported aspartic acid as the important form of nitrogen excreted from legume nodules.

In some preliminary tests with several organic nitrogen compounds, evidence was obtained of asparaginase and urease activity by the exoenzymes of corn roots. These experiments were not carried far enough to warrant a report at this time, but an effective dephosphorylation of nucleic acid and a positive qualitative test for asparaginase and urease activity by corn roots reopen the question of direct absorption of organic nitrogen.

SUMMARY

A microscopic examination of the cellular materials released by roots to the rhizosphere during their normal growth process was made. This residue was composed largely of well-nucleated, intact cells, which underwent considerable swelling and elongation soon after being released from the root proper. There was some evidence of rupture and release of the contents of a few of these cells under the conditions of solution culture that were maintained in these tests, but the bulk of the cells appeared to maintain a well-preserved condition for a considerable period after detachment.

The previous level of phosphorus nutrition of corn and tomato plants had no measurable effect on the nuclease activity of their roots. The roots of phosphorus-starved plants exhibited a slightly higher glycerophosphatase activity than those of plants that were given ample phosphorus for 8 days prior to the tests.

The glycerophosphatase system of corn roots had an optimum reaction of pH 4.0 at a temperature of 27°C. in 12-hour tests. Maximum activity of the same system was obtained at 45°C. (pH 4.0) in 9-hour tests.

Optimum pH for the nuclease system of corn roots, as measured by release of inorganic phosphorus at 27°C. in 12 hours, was about 6.3. Maximum activity of this system was obtained at 60°C. when a pH of 7.0 was maintained for 12 hours.

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THE OCCURRENCE AND ORIGIN OF UREASELIKE ACTIVITIES IN SOILS[1]

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That microorganisms are directly responsible for the chemical transformation of every organic substance in soils has been the prevailing opinion among soil scientists for many decades. This concept has been fostered, undoubtedly, by the paucity of data pointing to the presence in the soil of any other agency capable of bringing about these transformations. One such transformation, the hydrolysis of urea, considered to be caused by the direct action of microorganisms in soils, has recently been shown (2, 4, 5) to take place by catalysis as well. In fact, in many soils studied, catalysis has proved to be the dominant factor in this transformation. Other evidence (3) indicates that the catalyst or catalysts responsible are similar to the enzyme urease, in most but apparently not in all of the properties studied. In view of the few published data bearing on the mere existence of any enzymatic activities in soils, our studies of the hydrolysis of urea by ureaselike catalysts were extended to the testing of soils from different locations and from various cropping treatments. In addition to the studies of their occurrence some attention has also been given to the possible origin of these ureaselike activities.

LABORATORY TECHNIC AND STOCK SOILS USED

For each 400-gm. sample of soil to be tested for ureaselike activity, a glass percolator was prepared by inserting a porcelain filter disk and filter paper. Percolations were carried on both in the presence and in the absence of toluene. In the former, the antiseptic was thoroughly mixed both with the soil (about 5 to 10 cc. per 400 gm. of soil) and with the percolating urea solution (in excess of saturation). The percolators, charged with soil, were placed in the incubator, which was maintained at approximately 30°C. Enough urea solution—100 to 200 cc.—was added to wet each soil initially and to bring it to the verge of dripping. Every 12 hours (in some cases 24) thereafter, during the test period, 75 cc. (unless otherwise indicated) of solution of the same concentration was added. Each percolate was transferred to another flask just before the addition of a new portion of percolating solution. The residual urea in each percolate was determined by Marshall's urease method essentially as described by Hawk and Bergeim (8), except that brom phenol blue was used as the indicator. Many of the percolates were too highly colored to permit the ready use of methyl orange.

The results are reported in milligram atoms of nitrogen per liter (m.at.N/liter).

On the assumption that the adsorptive capacity of a soil for urea was largely satisfied early in the percolation period, the reductions in concentration after the first and second percolates have passed through the soil may be looked upon as a more or less direct measure of the ureaselike activity of the soil in question.

The classification and history of the stock soils used are given in table 1.

TABLE 1

Classification and history of stock soils tested for ureaselike activity

SOIL NUMBER	SOIL TYPE	LOCATION IN CALIFORNIA NEAR	CROPPING TREATMENT	PREVIOUS HISTORY AND OTHER DATA*
C-17	Vina loam (14)	Chico	Weeds	Taken from railroad right of way
C-33	Vina loam (9)	Red Bluff	Orchard grass	As a cover in prune orchard
C-34	Maywood silty clay loam (9)	Corning	Olive nursery	General fertility low
C-62	Yolo silt loam (6)	Davis	Wheat	In various experimental crops
C-64	Yolo loam, deep subsoil (12)	Davis	Orchard	From an excavation below 8 feet
C-68	Yolo fine sandy loam (6)	Davis	Fallow	From 2nd foot of depth, in various experimental crops
C-70	Sacramento fine sand, deep sub-soil (12)	Broderick		From an excavation below 12 feet
C-81	Huerhuero sandy loam (1)	San Miguel	Fallow	Dry-farmed to grain since 1890
C-82	Nacimiento clay loam (1)	San Miguel	Fallow	Adjoining C-81, cropped but once since virgin condition
C-83	Linne clay loam (1)	Shandon	Wheat	Dry-farmed to grain since 1911

* All lots collected were surface soils unless otherwise specified.

CATALYTIC ACTIVITIES IN STOCK LOTS OF SOIL

Each of the stock lots of soils listed in table 1 was tested by the laboratory technic described. Figure 1 shows the results of percolation with several of these soils. As shown in figure 1 (left), soils C-64, C-68, and C-70 exhibited rather high initial adsorptive removal of urea and nearly constant but low catalytic activity thereafter. Soil C-83 showed low initial adsorption, with a rapidly rising type of catalytic activity. Soil C-82, which contained much organic matter, showed a high but slowly rising activity. In figure 1 (right) are given the results of percolations for three additional soils with some evidence of the reproducibility of results. One percolator for each of the soils in figure 1 (left) and those marked *a* in figure 1 (right) were held in the incubator at the same time. Those marked *b* and *c* were percolated simultaneously.

CATALYTIC ACTIVITY IN SELECTED SOIL SAMPLES

The differences in activity found between soils C-81 and C-82 and among other samples suggested that the presence of organic matter, especially that of rather

recent origin, might be associated with the higher activities found.   This sugges-
tion was strengthened by data from a preliminary experiment on two portions
of soil C-68, which had been carried forward in the greenhouse.   One, moistened
to about field capacity, had been incubating in covered crocks for approximately
16 months; the other had been cropped in large pots almost continuously for 2
years—in winter to oats, and in summer to milo.   The urea-splitting activity
of the incubated soil was reduced to less than half its original value.   On the
other hand, the growing of the crops resulted in about a threefold increase over
the original activity.
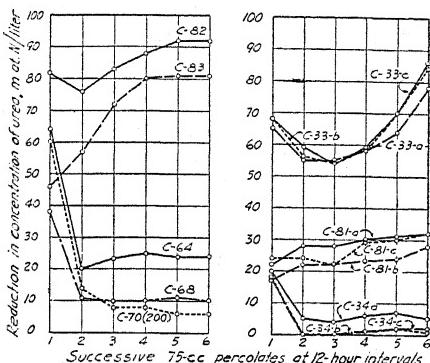
FIG. 1   FIG. 2

FIG. 1. REDUCTION IN INITIAL CONCENTRATIONS OF UREA SOLUTIONS PERCOLATED IN THE
PRESENCE OF TOLUENE THROUGH 400-GM. SAMPLES OF VARIOUS STOCK SOILS

The initial concentration was 100 m. at. N/liter for all soils except C-70, for which the
concentration was 200 m. at. N/liter

FIG. 2. REDUCTION IN INITIAL (200 M. AT. N/LITER) CONCENTRATION OF UREA SOLUONITS
PERCOLATED IN THE PRESENCE OF TOLUENE THROUGH 400-GM. SAMPLES COLLECTED AT
VARIOUS DEPTHS FROM TWO ORCHARDS

These tests, of course, require more general confirmation, but the implications
to be drawn from them are of interest.   The chemical substances responsible
for these ureaselike activities probably undergo decomposition slowly under
favorable conditions of temperature, moisture, and aeration.   In consequence,
the substances actually present at any one time may gradually diminish and may
almost disappear over a period of years.   Cropping, or some related factor,
seems to increase this activity.   In a cropped soil both losses and gains may occur
simultaneously.   With a uniformly cropped soil, therefore, we may expect the
activity to tend toward an equilibrium governed particularly by the existing soil
and cropping conditions.

With these implications in mind, samples of soil for test were taken from loca-
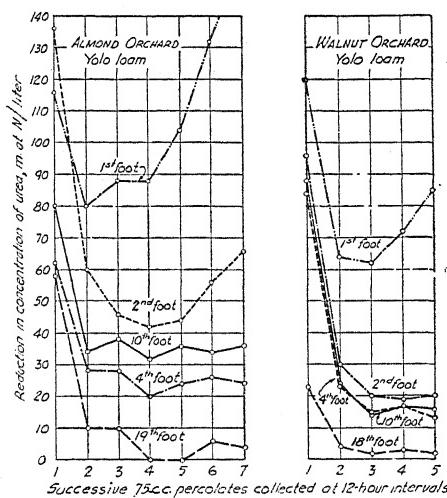
TABLE 2

Reductions in concentrations of urea solutions percolated through samples* of soils from different locations and under contrasting cropping treatments

Values in m. at. N/liter

SOIL AND CROPPING TREATMENT	ANTISEPTIC PRESENT DURING PERCOLATION	ORIGINAL UREA CONCEN-TRATION	REDUCTION IN CONCENTRATION OF UREA IN SUCCESSIVE 75-CC. PERCOLATES COLLECTED AT 12-HOUR INTERVALS					
			1	2	3	4	5	6
Yolo loam (12)								
Bermuda	Toluene	400	198	128	112	140	174	224
	None	400	228	86	114	370	396	398
Fallow (no weeds)	Toluene	400	170	66	74	106	132	154
	None	400	140	110	50	78	314	396
Fallow (heavy morning-glory)	Toluene	400	188	108	112	166	196	236
	None	400	150	90	94	314	400	400
Shade trees (clean-culti-vated)	Toluene	400	168	152	114	110	120	138
	None	400	226	240	342	394	400	400
Bluegrass lawn	Toluene	400	378	400	398	388	388	384
	Toluene	1600	900	810	1280	1020	810	610
Kikuyu grass—no tops	Toluene	400	194	148	176	244	362	398
	Toluene	1600	700	350	970	1450	710	730
Kikuyu grass—tops in-cluded	Toluene	400	196	376	398	400	400	400
	Toluene	1600	660	580	1530	1490	1090	800
Yolo silt loam (6)								
Bent grass lawn	Toluene	400	168	108	98	108	102	108
Burnet meadow	Toluene	400	172	84	90	122	116	150
Fallow (heavy morning-glory)	Toluene	400	210	100	92	132	146	160
	None	400	172	218	304	388	398	400
Fallow (no weeds)	Toluene	400	186	56	46	48	60	90
	None	400	168	96	46	46	70	154
Yolo clay loam and clay (12)								
Bluegrass sod	Toluene	400	292	254	254	288	324	358
Clump of privet	Toluene	400	316	202	224	278	316	328
Pasture—unirrigated	Toluene	400	320	184	160	216	304	366
Alfalfa—surface foot	Toluene	400	306	214	190	248	324	394
	None	400	346	118	380	394	396	398
Alfalfa—third foot	Toluene	400	318	190	150	164	170	186
	None	400	340	194	186	392	398	398
Yolo fine sandy loam (6)								
Pasture	Toluene	100	20	12	12	13	14	14
Pasture (heavy star thistle)	Toluene	100	48	37	35	33	33	38
Uncultivated	Toluene	100	49	36	38	46	48	57
	Toluene	400	152	86	66	94	106	138
	None	400	138	96	88	114	400	400
Weeds—including tops	Toluene	100	95	97	100	99	99	99
	Toluene	400	302	260	266	286	286	340
	None	400	272	326	394	394	394	400
Bermuda sod	Toluene	100	63	61	52	52	54	56
	Toluene	400	140	86	78	82	88	98

TABLE 2—*Continued*

SOIL AND CROPPING TREATMENT	ANTISEPTIC PRESENT DURING PERCOLATION	ORIGINAL UREA CONCEN-TRATION	REDUCTION IN CONCENTRATION OF UREA IN SUCCESSIVE 75-CC. PERCOLATES COLLECTED AT 12-HOUR INTERVALS					
			1	2	3	4	5	6
Fargo clay (11)								
Rotation 6B with millet	Toluene	200	186	108	82	54	42	42
	None	200	183	129	137	171	196	198
Rotation 5B with sweet	Toluene	200	190	144	94	66	58	56
clover	None	200	181	153	154	198	198	199
Sites gravelly sandy loam (12)								
Fallow (alternate grain)	Toluene	200	37	27	21	23	19	..
	None	200	51	26	32	35	41	39
Adjoining fence row	Toluene	200	83	93	98	168	158	..
	None	200	72	80	134	185	198	199
Fence row burned	Toluene	200	58	51	50	50	54	55
	None	200	60	62	70	77	101	132
Yolo loam and clay loam (12)								
Winter Nelis pears								
Clean cultivated	Toluene	200	120	66	72	92	114	136
	None	200	109	59	49	49	55	56
In rye-grass sod	Toluene	200	166	156	188	196	198	198
	None	200	150	126	162	194	198	196
Cover crops in plum or-chard								
None (check)	Toluene	200	130	46	36	50	72	86
Alfalfa (nearly perma-nent)	Toluene	200	158	146	186	196	198	200
Hubam clover (sum-mer)	Toluene	200	128	92	108	120	136	154
	None	200	113	71	66	74	108	160
None (check)	Toluene	200	108	50	52	52	60	74
	None	200	108	53	37	40	49	65
Melilotus indica	Toluene	200	116	78	80	94	110	146
	None	200	119	63	60	64	86	132
Rye (winter)	Toluene	200	128	80	86	100	116	166
	None	200	128	69	61	68	77	153
None (check)	Toluene	200	118	60	78	84	94	106
	None	200	118	49	38	39	43	52

* Weight of each sample, 400 gm.

tions for which the same or similar cropping treatments had probably prevailed for several years. Each of these soil samples, of 1 to more than 4 kgm., was air-dried immediately after being taken from the field, then was broken up, sieved, and mixed.

Table 2 reports the activities found in these soil samples together with the variations from the standard percolation procedure used. Samples of all soil types under the various cropping treatments, except Fargo clay, were collected near Davis, California. Fargo clay was from the experimental rotation plots

of the North Dakota Argicultural Experiment Station: 5B from a rotation of corn, barley, clover (or sweet clover), and wheat; and 6B from a rotation of corn, barley, timothy (or millet), and wheat.   The order of plots of cover crops in the plum orchard in the field is the same as that given in table 2 (13).   Some samples of soil showed greater activity in the absence of toluene; others, greater activity in its presence.   No satisfactory explanation of these differences is now apparent.

The results in table 2 indicate that the addition of some types of organic matter may increase the activity of a soil.   Furthermore, the table suggests that samples from deeper soil levels have less activity than samples from the surface, which, as is well known, are generally higher in organic matter.

Further evidence of the relative activity of soils at various levels in a few soil profiles was obtained during the 1940 season on samples collected from available
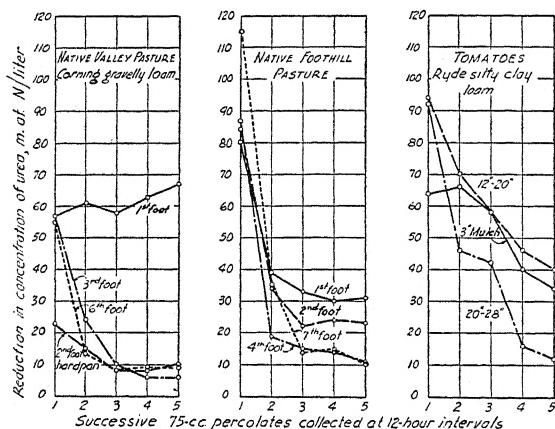
FIG. 3. REDUCTION IN INITIAL (200 M. AT. N/LITER) CONCENTRATION OF UREA SOLUTIONS PERCOLATED IN THE PRESENCE OF TOLUENE THROUGH SAMPLES COLLECTED FROM VARIOUS DEPTHS AND FROM DIFFERENT AREAS

The Corning and the pasture soil samples weighed 400 gm.; the Ryde soil, 250 gm.

excavations.   The activities found in samples from mature orchards of almonds and English walnuts near Davis, California, are plotted in figure 2.   Figure 3 shows the activities in soil profiles from areas in California away from Davis. The Corning gravelly loam (10) samples were collected about 10 miles east of Sacramento.   The samples (soil not mapped) from the native foothill pasture were from about 1 mile north of Folsom.   The samples of Ryde silty clay loam (7) were from the north end of Staten Island.   The Ryde soil, approaching a muck in organic matter content, had been in a variety of field and vegetable crops for many years.   Because of its lighter volume weight, only 250 gm. of each sample of this soil was used in the percolator instead of the usual 400 gm.   In general, the results show that the deeper the sample from the soil profile, the less the activity, although certain local reversals of this principle have been observed.

ORIGIN OF THE ACTIVITIES

Processes involved in cropping

Further samples of the cropped and the incubated lots of Yolo fine sandy loam, C-68, studied in a previous experiment, were investigated to determine the origin of their ureaselike activity. Each lot was dried, sieved, and mixed before being tested. Data on the successive percolates collected are plotted in figure 4 (left), which shows that incubation reduced the activity one half or more, whereas cropping increased the activity to about four times the original value for this soil. The preheated lot (2) of this original soil gave only negligible activity.
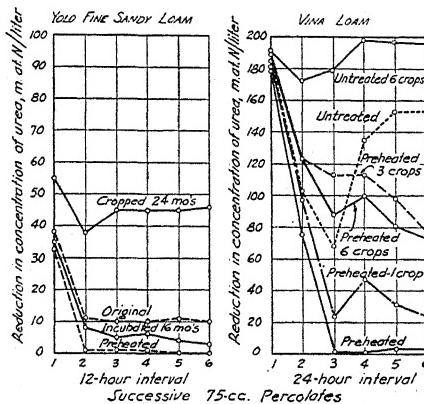
FIG. 4. REDUCTION IN CONCENTRATIONS OF UREA SOLUTIONS PERCOLATED IN THE PRESENCE OF TOLUENE THROUGH 400-GM. PORTIONS OF TWO SOILS AS INFLUENCED BY VARIOUS CROPPING, PREHEATING, AND INCUBATION TREATMENTS

Figure 4 (right) shows the activities determined from percolating lots of Vina loam, C-17, previously subjected to treatments in an experiment with other objectives. In these tests the successive portions of the percolating solution were added at intervals of 24 hours. With the untreated (i.e., unheated) soil, six successive crops of milo considerably increased the activity. Again, preheating the soil reduced the activity to negligible amounts, presumably by destroying the enzyme. Cropping or processes associated with it, however, increased the activity of the preheated soil. The increase was considerable, following one crop, and still more, following three and six successive crops.

The method of cropping the preheated soil, used in obtaining the data in figure 4 (right), was extended to other crops on another soil. Two 1-gallon crocks, each containing 4 kgm. of Yolo silt loam, C-62, preheated to 85°C., as previously described were planted to each of a number of crops, and eight 5-inch pots, each containing 1 kgm. of the original untreated soil, were similarly planted for the same growing period. Table 3 gives the yields of the green weight of these crops.

Figure 5 plots the results of the percolation trials with these cropped lots of soil. In figure 5 (left) appear data from five of the cropped lots of the soil previously preheated and from two lots of untreated soil cropped respectively to pumpkins and buckwheat. The concentration of urea used in these seven lots of soil was 100 m.at.N/liter. Although the original untreated soil did not
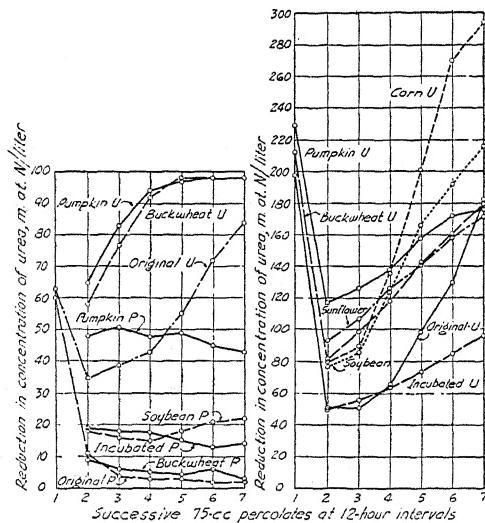
Fig. 5. Reduction in Concentrations of Urea Solutions Percolated in the Presence of Toluene through 400-gm. Portions of Yolo Silt Loam, C-62, as Influenced by Previous Preheating and Cropping Treatments

U = untreated soil; P = preheated soil

TABLE 3

Yield of green weight of crops grown as cropping treatments affecting the catalytic activities shown in figure 5

Green weight in grams per vessel

CROP	YIELD FROM 1,000 GM. UNTREATED SOIL; AVERAGE OF EIGHT POTS	YIELD FROM 4,000 GM. PREHEATED SOIL; AVERAGE OF TWO CROCKS
Buckwheat............................	7.9	102.5
Corn.................................	13.9	291.5
Pumpkins.............................	32.2	247.8
Soybeans.............................	12.6	85.0
Sunflowers...........................	15.0	82.2

remove all of the urea from solution, the untreated soil cropped to pumpkins and buckwheat did remove virtually all from the fifth and later percolates. After incubating for 2 months, the preheated soil showed increased activity. Presumably the cropped preheated soil went through similar processes in addition to those strictly related to cropping. Any increase in activity attributed to cropping should be greater than that of the incubated preheated soil.

With the cropped lots of untreated soil, a higher concentration of urea was necessary, hence 400 m.at.N/liter was used. As will be observed, incubating the untreated soil for 2 months somewhat decreased its activity. Perhaps compounds responsible for these activities were decomposed to a certain extent, a process that we might infer took place as well in the cropped soils, since these were wet nearly as much and were at comparable temperatures. If such was the case, cropping the untreated soil to each of the plants named considerably increased the activities.

Addition of organic materials

Though the data are conclusive that the total of all the processes involved in cropping have, in general, increased the ureaselike activities of these soils,
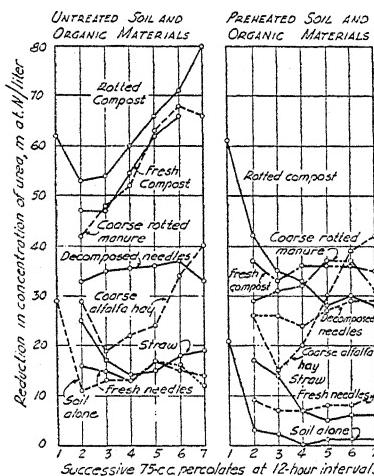
FIG. 6. REDUCTION IN THE CONCENTRATIONS OF UREA SOLUTIONS INITIALLY CONTAINING 100 M. AT. N/LITER PERCOLATED IN THE PRESENCE OF TOLUENE THROUGH 400-GM. PORTIONS OF YOLO FINE SANDY LOAM, C-68, TO WHICH VARIOUS ORGANIC RESIDUES HAD BEEN ADDED

Some of the values for the first percolates were omitted to avoid confusion of lines

still it is not clear just what factor or factors related to it are responsible. The plant tissues themselves might have contained the enzyme, urease, which would diffuse out of ruptured or dead cells to enhance urea hydrolysis. Microorganisms causing decay of the plant residues may have formed the enzyme. The growing plants may have liberated the enzyme to the soil.

Many plants, especially soybeans and the jackbean, are known to contain urease. In the sugar beet rotation experiments reported earlier (4) the addition of manure to the soil enhanced the activity materially. To determine the effect of plant residues on the ureaselike activities of soils, $13\frac{1}{2}$ gm. of each of the following materials was added to respective 400-gm. portions of both the untreated and the preheated lots of Yolo fine sandy loam, C-68: rotted leaf compost 18

months old; fresh leaf compost 6 months old; rotted barnyard manure several years old; coarse alfalfa hay consisting mostly of leaves; fresh needles of *Pinus ponderosa*; partly decomposed needles of *P. ponderosa*; and oat straw. The resulting effects are shown in figure 6.

Figure 7 shows additional data obtained with some of these materials likewise added to untreated and preheated soil, both in the presence and in the absence of toluene. In the interim, the lots of the alfalfa hay and the well-rotted manure were finely ground in a Wiley mill.

Eight milligrams of jackbean urease added to 400 gm. of untreated soil without toluene showed a rising activity with continued percolation. On preheated
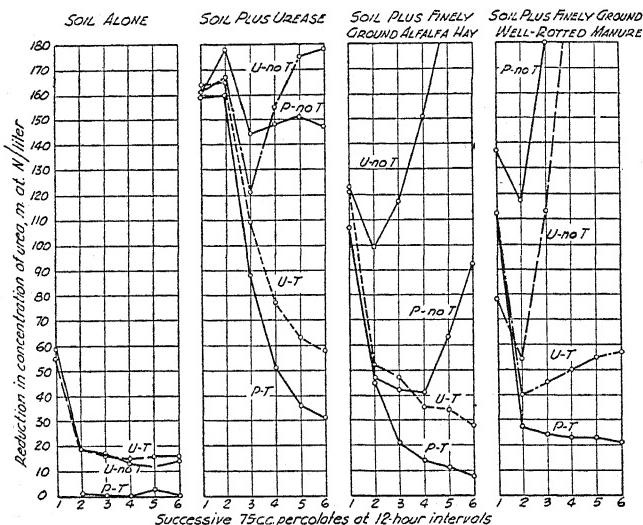
FIG. 7. REDUCTION IN INITIAL (200 M. AT. N/LITER) CONCENTRATION OF UREA SOLUTIONS PERCOLATED THROUGH 400-GM. PORTIONS OF YOLO FINE SANDY LOAM AS INFLUENCED BY NATURE OF ORGANIC MATERIALS ADDED, BY PREHEATING OF SOIL, AND BY PRESENCE OF TOLUENE DURING PERCOLATION

U = untreated soil; P = preheated soil; T = toluene present during percolation; no T = no toluene present during percolation

soils, however, the activity was rather uniform—an interesting fact, indicating that urease added to a soil (preheated and therefore with negligible activity) produced a fairly stable activity. The rise of activity with the untreated soil may be attributed to some property of that soil itself, or to the interaction of the soil, urea, urease, and the products of urea hydrolysis. Of interest also are the declines in activities of urease added to untreated and preheated soils, percolated in the presence of toluene as compared with the activities without toluene. Formerly this decline of activity of added urease was attributed (3) to the greater lability against decomposition as compared with the native activity of the soil. It would appear in the light of these data that jackbean urease is unstable in the presence of toluene and at least comparatively stable in its absence.

Incubation of organic materials

The crop residues presumably might, by stimulating microorganisms, cause the production of microbial enzymes, which in the presence of toluene might still function in transforming urea. To test this hypothesis, each material and combination of materials listed in table 4 was added to 3 kgm. of preheated Yolo

TABLE 4

Reductions in concentrations of urea solutions percolated through samples of preheated Yolo silt loam C-62 as influenced by materials added previous to incubation and by presence or absence of toluene during percolation*

Results in m.at.N/liter

AMENDMENTS BEFORE 2-MONTH INCUBATION	REDUCTION IN CONCENTRATION OF UREA IN SUCCESSIVE 75-CC. PERCOLATES COLLECTED AT 12-HOUR INTERVALS						REDUCTION IN CONCENTRATION OF UREA IN SUCCESSIVE 75-CC. PERCOLATES COLLECTED AT 12-HOUR INTERVALS					
	1	2	3	4	5	6	1	2	3	4	5	6
	Percolated without antiseptic						*Percolated with toluene*					
None..................	112	36	20	16	12	12	98	30	24	24	14	10
Calcium nitrate........	182	50	18	12	8	8	190	40	28	22	16	14
Urea..................	106	28	10	8	2	6	96	22	26	18	8	8
Gelatin................	104	26	16	16	12	10	92	22	26	22	10	12
Sucrose...............	132	58	40	42	76	142	118	74	66	57	51	37
Sucrose and calcium nitrate..............	172	80	70	70	86	122	162	91	94	80	56	46
Sucrose and urea.......	102	36	18	16	14	12	88	34	26	28	16	10
Sucrose and gelatin....	108	34	20	18	8	16	94	36	36	26	14	8
Straw.................	150	86	80	58	58	92	128	42	54	46	26	22
Straw and calcium nitrate................	186	108	72	64	64	102	194	94	76	58	46	36
Straw and urea........	140	78	142	196	196	196	120	68	54	40	40	28
Straw and gelatin......	80	118	96	110	176	196	142	108	102	98	86	76
Nucleic acid...........	106	34	20	20	16	16	98	28	26	22	14	14
Casein................	110	30	14	14	12	14	100	22	22	24	10	8
Egg albumin...........	40	68	36	20	18	16	100	28	26	20	14	10
Heat-dried alfalfa......	144	90	74	68	70	138	156	122	118	106	84	78
Control:												
Unheated soil—unincubated............	116	46	36	36	34	46	112	46	54	68	76	96
Unheated soil—incubated..............	..	..	..	..	..	..	110	38	46	48	44	52

* Urea concentration of solution, 200 m. at. N/liter; weight of soil sample, 400 gm.; 2-month incubation at 30°C.

silt loam, C-62, in 1-gallon covered crocks. The amount of urea, gelatin, nucleic acid, casein, egg albumin, alfalfa, or calcium nitrate added was in each case calculated to contain 150 m.at.N/crock; the amount of sucrose added was sufficient to give 2,000 m.at.C/crock; and oat straw was added at the rate of 100 gm. per crock.

Difficultly soluble materials, finely pulverized and dry, were thoroughly mixed

with the dry soil.   Water-soluble materials were dissolved in the 900 cc. of distilled water necessary to wet the soil.   All incubated soils were wetted.   After incubating for 64 days at 30°C., the soils were dried at temperatures less than 50°C., broken up, mixed, and stored.   One 400-gm. subsample of each was subjected to percolation in the absence of toluene as described above, and another subsample was percolated with toluene present.

Incubation of the soil with each of the nitrogen-containing amendments singly, caused no material increase in activity.   Among those receiving sucrose and sucrose plus some carrier of nitrogen, only in the lots receiving sucrose alone or sucrose plus calcium nitrate were the activities noticeably increased.   The activities in the others may have reached a peak during incubation and then declined, or some chance step in the technic may have caused these differences.

As table 4 reveals, the decay of oat straw alone increased the activity only a little, but straw plus, in turn, $Ca(NO_3)_2$, urea, and gelatin increased the activities still more.   Again perhaps the stage in the decomposition process selected for sampling was most important in determining the activities observed.   Alfalfa, dried at 85°C. or above, likewise developed considerable activity during incubation in the soil.

The percolation without toluene of subsamples of soil incubated with various energy materials, especially when these were of carbonaceous but not rapidly disappearing types, resulted in very rapidly rising activities.   These activities may, at present, be best attributed to a rapid increase in urea-decomposing organisms stimulated by media favorable for their multiplication and active metabolism.

From the data so far presented it is certain that incubation of some materials which themselves contain very little or no activities has caused activities of considerable magnitude to arise in the soil.

DISCUSSION

According to the data available (4) the catalytic activity causing the hydrolysis of urea in soils is related to the organic matter content, especially if recently added.   These data are entirely consistent with the view that the catalytic activity is caused by an enzyme or enzymelike substance or substances present in the soil.

Incubation of the soil over a period of months would be expected to reduce by decomposition the enzymelike substance responsible, whereas cropping might be expected to increase it.   Evidence to support both these expectations has been presented in these studies (cf. figures 4 and 5).

Cropping might have increased the catalytic activity of the soil through:

The direct additions of plant residues containing urease or similar urea-splitting enzymes or their precursors.

The formation of urease or ureaselike substances following the stimulation of microbial growth by the addition of plant residues.

The direct liberation within the soil of urease or ureaselike substances by the growing plants.

Evidence directly supporting the first two ways in which the ureaselike activities in soils may have originated have been presented herein (cf. figures 6 and 7, table 4). No evidence is available as to the direct liberation of urease or similar substances by the plants within the soil. It is now apparent that ureaselike activities found in soils may owe their origin, on the one hand, to the direct addition of urease or similar constituents to the soil from plant cells and, on the other hand, to the development of ureaselike substances by microorganisms from plant residues which contain little or none of these activities in themselves. These views are consistent with data presented in the first part of this paper on the occurrence of these activities as influenced by cropping treatments and depths in the soil profiles.

SUMMARY

In a continuation of an investigation of a thermolabile, enzymelike catalyst or catalysts which cause the hydrolysis of urea in soils, the occurrence of these ureaselike activities in cultivated and uncultivated soils was studied further. The technic was to determine the reduction in concentration of standard urea solutions percolated through portions (usually 400 gm.) of soil under constant temperature conditions and in the presence of toluene. Successive equal increments of the urea solutions were added to each percolator under test at equal (usually 12- or 24-hour) intervals. The successive percolates collected separately were analyzed for urea. After the rather small adsorptive capacity of the soil for urea was satisfied, generally from the first and second increments of solution added, the reduction in the original concentration of urea was taken as a criterion of the catalytic activity of the soil sample under test.

Several stock lots of soil were tested together with specially selected soil samples representing contrasting cropping conditions or different depths in several soil profiles. Low to high initial adsorptive capacities were exhibited by the different soils. The catalytic activities were also varied. Generally soils of low ureaselike activity were nearly constant with continued percolation, whereas those of a high ureaselike activity were of a rapidly rising type with the extension of the percolation period. Some exceptions were noted. Higher ureaselike activities were, in general, exhibited by soils with more organic matter and by soil with plant covers such as sods, pastures, and cover-cropped and weedy areas. These areas were supporting greater amounts of plant growth and therefore had a greater return of fresh organic matter to the soil. In soil profiles the surface foot almost invariably exhibited higher ureaselike activities than did lower levels. The activities in general decreased with depth, though several local exceptions did occur.

Preliminary experiments conducted under more carefully controlled conditions in the greenhouse disclosed markedly increased ureaselike activities in pots of soil intensively cropped for several months. The same original soil incubated moist showed a considerable loss of activity. Yolo silt loam preheated to destroy any ureaselike activity and the same soil untreated were both subjected to cropping in greenhouse studies. Increased activities following cropping with

some crops were evidenced by the subsequent percolation trials. The increase of activities occasioned by cropping may have arisen from the addition of plant residues containing urease or some of its more or less immediate precursors, the activities of microorganisms forming urease or similar substances during decomposition of the plant residues, and direct release of urease from the roots of the crop to the soil. No evidence in support of the direct release by the plant has been uncovered. Plant residues including jackbean urease, pine needles, coarse alfalfa hay, oat straw, barnyard manures, and leaf composts when added to soil increased its activity noticeably to markedly. Likewise, the ureaselike activities were much increased in many cases by the 2-month incubation of respective lots of preheated Yolo silt loam to which had been added various materials, such as oat straw, sucrose, starch, urea, nitrate, gelatin—substances themselves lacking or low in ureaselike activities. Presumably, the ureaselike activities originated from the increased growth of microorganisms during the incubation period.

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NITROGEN CONSERVATION OF NIGHT SOIL IN CENTRAL CHINA: I. CHANGE IN NIGHT SOIL, FECES, AND URINE ON STORAGE

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Night soil has been used as a manure in China for more than two thousand years, yet the practices involved in its collection and utilization are antiquated and may be expected to result in the loss of a considerable part of its nitrogen, which is agriculturally the most important, as well as the most variable, constituent of the human excreta.

The economic importance of night soil to Chinese agriculture has been stressed by many writers (1, pp. 23, 265; 3, p. 193; 8). Without it, Chinese agriculture could scarcely continue at the present level of production. Detailed figures concerning the amounts of night soil utilized and its monetary value are, however, difficult to obtain, those available being of doubtful accuracy. According to the data of the Szechwan Provincial Agricultural Institute, the city of Chengtu alone (population, 700,000) produces some 200,000 metric tons of night soil annually.

Chengtu belongs to the Szechwan rice area. The practice of using night soil in this area may be considered representative of practices in other parts of Central and South China. The farmers, from long experience, know that it is desirable to allow the fresh night soil to undergo a certain amount of decomposition and to dilute the material before applying it to the growing crops. It may be kept from two or three days to several months, according to the demand. The extent of dilution varies from one to ten parts of water to one part of night soil, more water being used with the solid excreta. Pits with sloping sides 1.5–2 x 1.5–2 x 1.5 meters, lined with a layer of cement, are used for storage of the night soil in the fields. Some of the pits are covered with thatched roofs, but many are uncovered and thus exposed to rainfall and sunshine.

Very little information is available concerning the processes involved in the storage of night soil (3, p. 193) and its use as manure or fertilizer. Wilson and Wang (7) have shown that, during a process of drying of the feces to cakes, 25 to 39 per cent of the nitrogen is lost, and that during the storage of these cakes as much as 50 per cent of the nitrogen is lost. The loss during storage for long periods could be cut about one half by keeping the cakes under cover. Kellner and Mori-no (4, p. 59) have shown that night soil loses nitrogen much more

rapidly in hot weather than during the cool season.   Chan (2) made a study of the effect of various chemicals, which were used to control hookworm, upon the loss of nitrogen from night soil during storage in South China.

Long periods of storage of night soil in pits in the open air are believed to result in the loss of a considerable part of the nitrogen.   The present study was made to obtain specific information concerning losses of nitrogen during prevailing methods of storage, with the objective of developing more effective means of utilizing the excreta as manure.   This paper is a preliminary report on some of the changes in nitrogen that occur during the storage of the night soil, as well as of the feces and urine when stored separately.

MATERIALS AND METHODS

Feces and urine, supplied by a commercial dealer and thus representative of the product obtained from the city population, and a night soil compounded of a mixture of the two in equal parts (natural night soil being variable in composition) were used in this study.   The materials were stored separately in glazed earthenware jars (*kangs*), 73 cm. deep and 42 cm. in diameter at the mouth, first widening and then tapering toward the bottom.   The jars were filled to about four fifths of their capacity with carefully mixed amounts of material.   They were placed, uncovered, against a brick wall and were protected from the sun and rain by a thatched roof, storage conditions in a roofed farm pit thus being simulated.

Samples were taken at weekly intervals during a 16-week storage period. Ammonia nitrogen was determined on fresh samples, whereas analyses for total nitrogen were made on dried samples.

Because of their obnoxious odor, the samples were partly dried out of doors (under a roof).   Twenty-five milliliters of concentrated HCl was added to each of the fresh samples before it was dried preparatory to the nitrogen determination.   Most of the water was driven off over a hot-water bath, and then the drying was finished in an oven.   The samples taken from November 27 to December 4 were dried in an outdoor oven, heated with an alcohol lamp; samples following that date, after partial drying in this oven, were finished in the laboratory, in an electric oven at 105°C. with much better temperature control.   The dried material was ground to powder and was again heated in the electric oven to make certain that all moisture was removed before the nitrogen determinations were made.

At the end of the experiment, the material remaining in the jars was weighed in order to calculate the loss in weight during storage; allowance was made for the samples that had been taken for analyses.

The moisture values fluctuated greatly.   This is ascribed to the variable temperature of the outdoor drying oven, since more consistent results were obtained after the electric oven was used to complete the drying process.   The total nitrogen values determined on the dried samples showed much less fluctuation and lower standard errors than the moisture contents.   The fluctuation in moisture determinations made the conversion of data between "dry" and "fresh"

values difficult. Consequently, only the determinations made on samples dried in the electric oven were used in the calculations. The general mean of the moisture content for each type of material was used as a conversion factor for that material.

RESULTS

The detailed results for feces are given in figure 1. The general form of the ammonia curve[2] indicates a rapid initial production of ammonia, followed by a decrease in the rate and then a slight increase toward the end. Conditions within the mass of feces were relatively anaerobic most of the time, even though the
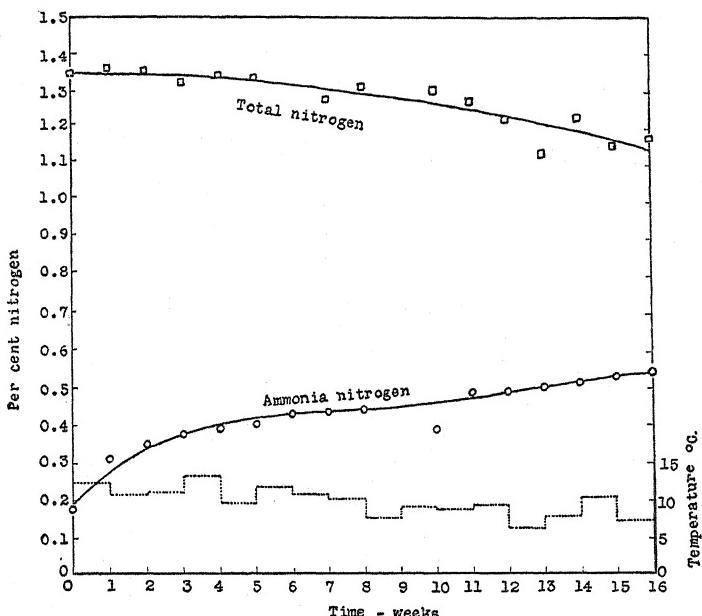
FIG. 1. CONCENTRATION OF TOTAL NITROGEN AND OF AMMONIA NITROGEN IN FECES DURING STORAGE

The broken line below indicates the mean air temperature

material was stirred weekly. This was evident from the strong odor of H_2S that came from the material when it was stirred. It appears likely that nitrogen was lost through volatilization of ammonia during the storage period.

The total nitrogen values were converted to the "fresh" basis for comparison with ammonia nitrogen. There appears to have been a comparatively uniform rate of loss of nitrogen after the first 4 weeks. During the early period somewhat less nitrogen disappeared. This is attributed to an increase in the ammonia content, which would have raised the pH and thus favored volatilization of the ammonia.

[2] Curves for total nitrogen and ammonia nitrogen values for feces, urine, and night soil were all fitted by Fischer's method of orthogonal polynomials as described by Snedecor (5, pp. 324–334).

TABLE 1

Changes in the dry matter and nitrogen* of feces, urine, and night soil during storage

DATE OF SAMPLING	PERIOD OF STORAGE	WEIGHT OF FRESH MATERIAL	WEIGHT OF DRY MATTER	TOTAL NITROGEN			AMMONIA NITROGEN		
				In fresh material	Weight	As per cent of original	In fresh material	Weight	As per cent of original
	weeks	gm.	gm.	per cent	gm.		per cent	gm.	
Feces									
Nov. 2.........	0	98.0	18.46	1.340	1.313	100.0	0.174	0.170	100
27.........	4	91.2	17.18	1.335	1.217	92.7	0.406	0.370	218
Dec. 25.........	8	84.5	15.93	1.296	1.095	83.4	0.446	0.377	221
Jan. 22.........	12	77.7	14.63	1.235	0.960	73.1	0.495	0.385	226
Feb. 19.........	16	71.0	13.38	1.173	0.832	63.4	0.550	0.391	230
Gain or loss.......	..	−27.0	−5.08	....	−0.481	−36.6	....	+0.221	+130
Per 100 gm. of original material..........	..	−27.6	−5.18	....	0.491	....	....	+0.226	....
Urine									
Nov. 2.........	0	98.5	1.67	0.204	0.201	100.0	0.266	0.262	100.0
27.........	4	94.3	1.59	0.186	0.175	87.1	0.209	0.197	75.3
Dec. 25.........	8	90.2	1.56	0.174	0.157	78.1	0.172	0.155	59.3
Jan. 22.........	12	86.0	1.45	0.133	0.114	56.7	0.139	0.120	45.8
Feb. 19.........	16	81.8	1.38	0.096	0.079	39.3	0.100	0.082	31.3
Gain or loss.......	..	−16.7	−0.29	....	−0.122	−60.7	....	−0.184	−68.7
Per 100 gm. of original material..........	..	−17.0	−0.29	....	−0.124	....	....	−0.187	....
Night Soil									
Nov. 2.........	0	112.5	9.37	0.698	0.785	100.0	0.156	0.176	100
27.........	4	109.4	9.11	0.648	0.709	90.3	0.261	0.286	162
Dec. 25.........	8	106.3	8.86	0.648	0.689	87.8	0.299	0.318	180
Jan. 22.........	12	103.1	8.59	0.648	0.668	85.1	0.316	0.326	185
Feb. 19.........	16	100.0	8.33	0.596	0.596	75.9	0.336	0.336	191
Gain or loss.......	..	−12.5	−1.04	....	−0.189	−24.1	....	+0.155	+91
Per 100 gm. of original material..........	..	−11.1	−0.92	....	−0.168	....	....	+0.138	....

* Percentages of nitrogen in fresh material given for sampling dates November 27 to January 22 inclusive are values calculated by Fischer's method of orthogonal polynomials; those given for November 2 and February 19 are experimental determinations.

The results for total and ammonia nitrogen presented in table 1 show that whereas 13 per cent of the nitrogen in the feces occurred as ammonia at the beginning, as much as 47 per cent was ammonia at the end of the storage period. Human feces, either fresh or stored, may therefore be regarded as a source of readily available nitrogen.

The detailed results for urine appear in figure 2. The results show an almost constant rate of loss of nitrogen with a slightly slower rate during the middle period. It is noteworthy that the initial ammonia content was the highest; there is no evidence of any production of ammonia from urea after the period of storage began. The urine was not perfectly fresh, and it may have stood for a day or so in latrines and commercial storage pits before it was delivered. It appears likely that the urea was already completely hydrolyzed at the time the experiment was
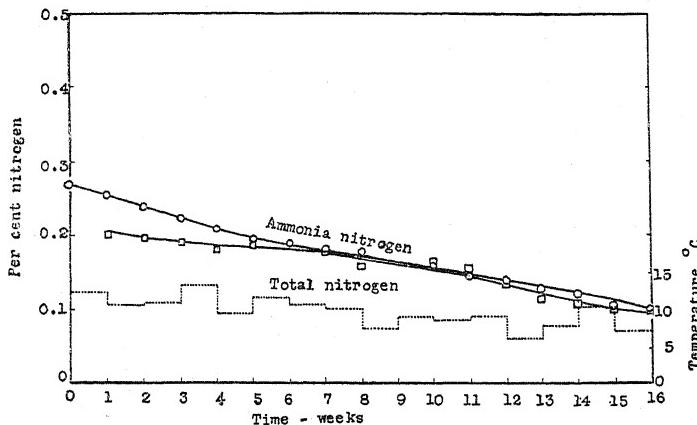
Fig. 2. Concentration of Total Nitrogen (Curve with Squares) and of Ammonia Nitrogen (Curve with Circles) in Urine During Storage
The broken line below indicates the mean air temperature

started. Urea-hydrolyzing organisms and enzymes are plentiful and very active in nature (6, pp. 161–162) and rapidly convert urea to ammonia.

The content of nitrogen in the urine was lower than that recorded by some other workers. Although there may have been some loss before the experiment was started, it seems likely that the urine was, in fact, low in nitrogen. It was collected during cool weather, when there is little perspiration; it came from a city where tea shops are abundant and well patronized. Both are factors that would tend to give a rather dilute urine.

The values for total nitrogen in the fresh urine are below those for ammonia nitrogen. This discrepancy is ascribed to inadequacy of the drying procedure, during which some of the nitrogen was doubtless lost, even though the material was at all times strongly acid as a result of the addition of HCl. The total nitrogen values should in all cases have been slightly higher than those for ammonia nitrogen. It may be concluded that virtually all the nitrogen in the urine was accounted for as ammonia at all storage periods.

The results for night soil are shown in figure 3. During storage, ammonia was produced at a relatively uniform rate. In this respect, the night soil was intermediate between feces and urine, as might be expected, since the night soil was a mixture of equal parts of these two. It is interesting to compare the mean for the ammonia nitrogen in feces and urine with the ammonia nitrogen in the night soil. As shown in figure 3, during the first 10 weeks less ammonia was produced in night soil than in the feces and urine stored separately. After this period, both types of material had virtually the same ammonia content. This appears to have been due principally to the less rapid loss of ammonia from night soil than from urine alone, doubtless because of slower diffusion.
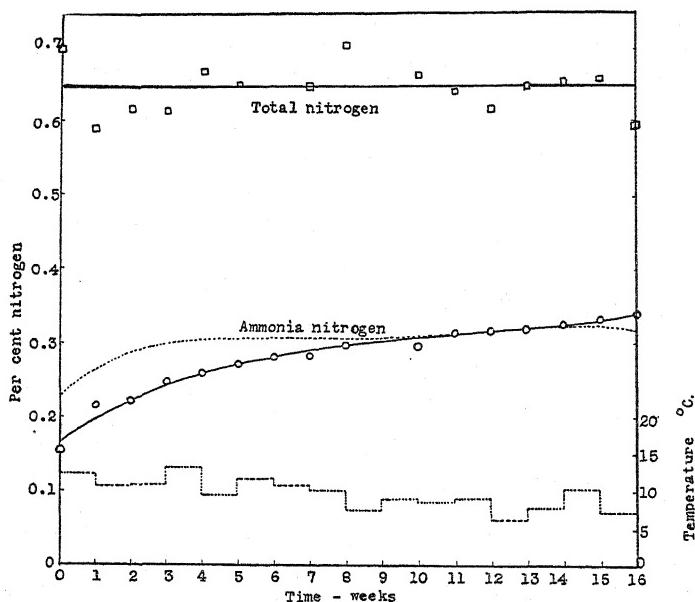
FIG. 3. CONCENTRATION OF TOTAL NITROGEN AND OF AMMONIA NITROGEN IN NIGHT SOIL DURING STORAGE

The dotted curve is the mean for ammonia nitrogen in feces and in urine stored separately. The broken line below indicates the mean air temperature.

From the "balance sheet" for total and ammonia nitrogen (table 1) it may be noted that whereas the original night soil contained 22 per cent of the nitrogen as ammonia, at the end of the period of storage 56 per cent of the nitrogen remaining was present as ammonia. This conversion took place at a fairly uniform rate. These results indicate that night soil supplies readily available nitrogen with less loss during storage than either urine or feces.

DISCUSSION

In considering the results it is important to note the season at which the investigation was carried out. The materials were stored during the late autumn

and winter months (November to February). These months are not so cold in Chengtu, however, as in many other parts of China. Indeed the mean temperature over the whole period was 9.65°C., which is rather moderate. During warmer seasons or in hotter localities, decomposition would have been more rapid and the transformation of nitrogen would have been completed more quickly, but it is believed that the course of the changes would have been much the same.

The losses in dry matter were 11 per cent for night soil, 17 per cent for urine, and 28 per cent for feces. The order was unexpected; it was anticipated that the loss from night soil would be intermediate between that of the urine and that of the feces. One factor favoring the conservation of organic matter in the night soil may have been its high moisture content: whereas the feces had 81 per cent moisture, the night soil contained 92 per cent. The greater compactness of the latter could have resulted in a slower rate of decomposition. There can be no doubt about the results, since they are based on direct weighings. Actually, this is a much smaller loss than would have been expected if the night soil behaved like the average of the separately stored feces and urine.

The losses of total nitrogen were similar to the losses of dry matter. Feces lost 0.491 gm. per 100 gm. of original fresh material, or 37 per cent of the original nitrogen. Urine lost 0.124 gm. per 100 gm. of original fresh material, but this was 61 per cent of the original nitrogen. The loss of nitrogen from urine was probably underestimated, since the loss of ammonia was greater than this. Night soil lost 0.168 gm. per 100 gm., or 24 per cent of the original nitrogen. These results suggest that from the point of view of reducing nitrogen losses on storage, it is better to keep human excreta in the form of the mixed night soil than to store the urine and the feces separately.

There were marked increases in the ammonia nitrogen in the feces and night soil, but a decrease of ammonia in the urine. In the urine, 0.187 gm. was lost per 100 gm. of original fresh material. This was 0.063 gm. more than the apparent loss of total nitrogen. The values for the percentage content of total nitrogen were lower than those for ammonia nitrogen, as a result of losses on drying of the samples before the determination of total nitrogen, and these losses were greater with the original urine than with the stored material. This reduced the apparent loss of total nitrogen on storage.

Similar losses of nitrogen may have taken place during the drying of feces and night soil samples, but they would be less apparent because of the higher proportion of total nitrogen as compared with the ammonia nitrogen in these materials.

The content of ammonia nitrogen in the feces increased 130 per cent on storage and 88 per cent in night soil. Most of this ammonia was produced during the first month in feces, but more slowly in night soil. If the urine present in the night soil had lost its ammonia as rapidly as when the urine was stored separately, one would have expected a gain of only 13 per cent in the ammonia nitrogen in the night soil. Thus it appears that the conditions in night soil were either more favorable to the production of ammonia or less favorable to its loss than were those in feces and urine stored separately.

The fresh feces used in this experiment contained over five times as much total nitrogen per unit weight as did fresh urine, but the urine contained one and half times as much immediately available nitrogen (ammonia). The night soil, being a mixture of equal parts of urine and feces, was intermediate between the two, with about one half of the nitrogen content of the feces. After 16 weeks' storage in open jars, in moderately cool weather, the stored feces had lost over one third of its original nitrogen, the stored urine had lost nearly two thirds; in the material remaining, the feces contained about 10 times as much nitrogen as the urine. The night soil lost only one fourth of its original nitrogen and was now nearly three fourths as concentrated as the feces. The ammonia nitrogen in the stored feces was more than double the original concentration; it now represented nearly one half of the total nitrogen. The ammonia nitrogen in the stored night soil was nearly double the original concentration; over one half of the total nitrogen of the stored material was present as ammonia.

These results have direct practical significance to the farmer who is buying, storing, and using human excreta. It is clear that the nitrogen of urine is readily available and is also easily lost. If urine and feces are collected separately, the urine should be used as soon as possible. The nitrogen of the feces is less readily available than that of the urine. The feces may be stored for a longer time than urine without such great losses. The actual loss of nitrogen, however, is high because of the higher total nitrogen content.

Although commercially and from the point of view of transport, there may be advantages in collecting and storing feces and urine separately, this practice results in excessive loss of nitrogen during storage. The night soil loses nitrogen relatively less rapidly than the separate materials. The use of night soil in ordinary farming, where long periods of storage are common, is thus to be preferred in order to conserve the nitrogen. These results apply to the humid parts of China, which is the rice region. Other considerations apply to the dry wheat region as well as in Yunnan Province and part of Kwangsi where the wet season is short and a long dry season is the rule.

SUMMARY AND CONCLUSIONS

In Szechwan, typical of Central China, either the separated urine and feces, or the mixed night soil, is used as manure. Because the materials commonly are stored for some time before use, the influence of storage on their composition was investigated.

Feces, urine, and a mixture of the two in equal parts in the form of night soil were stored in large jars for 16 weeks during cool weather under conditions similar to those on farms. Samples were analyzed weekly for moisture, total nitrogen, and ammonia nitrogen content. Losses in weight of the materials during storage were measured.

Changes in percentage nitrogen content in the stored materials were relatively small, although they amounted to more than half of the urine nitrogen. Ammonia nitrogen increased rather rapidly in the feces, less rapidly in the night soil, and decreased steadily in the urine.

Over the whole period of storage, the losses in dry weight were 28, 17, and 11 per cent for the feces, urine, and night soil respectively. The nitrogen losses were 0.491, 0.124, and 0.168 gm. respectively per 100 gm. of original material. The "percentage conservation" of total nitrogen was 76 for night soil, 63 for feces, and 39 for urine. Thus it seems that when human excreta, intended for use as manure, must be stored for any length of time, it is better, at least in the humid parts of China, to keep the material as the mixed night soil rather than separately as feces and urine.

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THE MOISTURE POTENTIAL OF SOILS

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Potential functions have been used for many years by soil physicists for evaluating the forces causing moisture movement. Edlefsen and Anderson, in a recent paper (5), have pointed out the advantages of the free energy concept in the thermodynamic interpretation of soil moisture measurements. In agreement with this viewpoint, it is proposed in the present paper to show the intimate relationships existing between the free energy and certain potential functions. The purpose of the study is to discover means for quantitatively comparing soil-moisture energy data derived from several different experimental techniques. Particular consideration will be given to the influence of solutes present in the liquid phase.

The mathematical details regarding the energy of retention of substances in heterogeneous systems were worked out by Gibbs in 1875 (7). Translated into modern symbols and terminology, the chemical potential was defined as follows:

$$\mu_i = \left(\frac{\partial F}{\partial n_i}\right)_{TPn_j} \tag{1}$$

where F is the free energy and n_i represents the amount of constituent i in the system in an appropriate unit of mass. The function μ_i therefore represents the change in free energy, at uniform temperature and constant pressure of each phase, brought about by the addition or removal of an infinitesimal amount of constituent i, all other constituents (j) remaining constant in amount during the process.

The chemical potential is identical with the partial molal free energy used by Lewis and Randall (11, p. 203) if the quantity n_i in equation (1) is expressed in moles. The term "chemical potential" is preferable because it allows free choice of the mass-unit. In the present paper the chemical potential of water will be expressed in ergs per gram and for convenience will be called the "moisture potential." The latter term was first suggested by Veihmeyer and Edlefsen (19).

Soil moisture is rarely in equilibrium in the field, but all methods of measuring potential functions require that the *measuring instrument* be in equilibrium with the soil at the point and time of measurement; consequently the properties of the moisture potential at equilibrium are important in soil moisture investigations. For example, consider a tall column of soil, free of solutes, in moisture-equilibrium with a water table at a considerable depth below the upper surface

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of the soil. The general condition for equilibrium of a species i in a gravitational field (8, p. 154) is

$$\mu_i^{\alpha} + \varphi^{\alpha} = \mu_i^{\beta} + \varphi^{\beta} \qquad (2)$$

where μ_i and φ refer to the chemical and gravitational potentials respectively, in ergs per gram, and the superscripts refer to any two positions α and β in the system. In the special case considered, the moisture and gravitational potentials will be arbitrarily set equal to zero at the water table. Equation (2) then reduces to

$$\mu = -\varphi \qquad (3)$$

where μ is the moisture potential at any given point in the soil and φ is the gravitational potential at that point. This is identical with the equation given by Israelsen (9, p. 487) for the "capillary potential."

For the purpose of studying soil-moisture energy relationships, a number of investigators have used the vapor-pressure method. This type of measurement will serve as a second illustration of the use of the moisture-potential function. From considerations dealing entirely with the thermodynamic properties of water vapor, it may be shown that the chemical potential of water in a mixture of perfect gases is

$$\mu = \frac{RT}{M} \log_e \frac{p}{p_0} \qquad (4)$$

where R is the gas constant in ergs per mole per degree, T is the absolute temperature, M is the molecular weight of water, p is the vapor pressure of water in the mixture and p_0 is the vapor pressure of pure water at the same temperature. Suppose a sample of soil is placed in a vessel in which the partial pressure of water in the gaseous phase is known or may be measured at the same horizontal level as the sample. The condition for equilibrium given in equation (2) reduces to

$$\mu_i^{\alpha} = \mu_i^{\beta} \qquad (5)$$

and it follows that when equilibrium has been reached the moisture potential in the soil is equal to the moisture potential in the gaseous phase, which in turn may be calculated from equation (4). This corresponds to the equation used by Edlefsen (4) for calculating the "capillary potential."

These examples indicate that in the two cases treated the moisture potential serves the same purpose as the capillary potential. The moisture potential, however, has the advantage of greater generality and, as will be seen from the following discussion, the results of most of the common experimental methods of studying soil-moisture energy relationships may be expressed in terms of the moisture potential.

THE OSMOTIC POTENTIAL

Most soils contain small amounts of soluble constituents. It will, therefore, be of interest to consider how the moisture potential is affected quantitatively by solutes dissolved in the liquid phase.

The properties of an aqueous solution are completely defined by the temperature T, the pressure P, and the mole-fractions N_j of the solutes. The variation of μ is given by the equation (8, p. 81)

$$d\mu = \left(\frac{\partial \mu}{\partial T}\right) dT + \left(\frac{\partial \mu}{\partial P}\right) dP + \sum_j \left(\frac{\partial \mu}{\partial N_j}\right) dN_j \qquad (6)$$

From the reciprocity relations (8, p. 35) the first two terms may be written $-sdT$ and vdP, respectively, where s is the partial specific entropy and v the partial specific volume of water. For simplicity the last term will be designated $d\omega$. Equation (6) then simplifies to give

$$d\mu = -sdT + vdP + d\omega \qquad (7)$$

where μ is the moisture potential in ergs per gram of water.

The quantity $d\omega$ in equation (7) may be evaluated for constant temperature and pressure by means of the Gibbs-Duhem formula (8, p. 15), to give the equation

$$(d\mu)_{TP} = d\omega = -\frac{1}{1000} \sum_j m_j d\mu_j \qquad (8)$$

in which m_j is the molality of the solute j and μ_j is the chemical potential of j in ergs per mole.

This equation may be integrated for certain simple cases to show the relationship between the composition of an aqueous solution and its moisture potential. For example, in a solution obeying Raoult's law at all temperatures and pressures (a "perfect" or "ideal" solution), the chemical potential of each solute species is related to its mole-fraction (11, p. 223) by the equation

$$d\mu_j = RT\, d \log_e N_j \qquad (9)$$

If the solution is dilute, the molality m_j may be substituted for the mole-fraction in this equation and, from the corresponding expression for $d\mu_j$, equation (8) may be integrated to give

$$\omega = -\frac{RT}{1000} \sum_j m_j \qquad (10)$$

where $\sum_j m_j$ represents the sum of the molalities of all solute species. The quantity ω, defined by its differential $d\omega$ in equation (8), has been termed the "osmotic potential" (12). Like the moisture potential, ω is arbitrarily set equal to zero for pure water. The osmotic potential of an aqueous solution, from its definition, is equal to the moisture potential. Therefore ω is a special

case of the moisture potential in which the reduction in activity of the water may be definitely attributed to "osmotic forces."

A second important application of equation (8) is the calculation of the osmotic potential of a nonideal binary solution. Pure uniunivalent salts, such as NaCl in water, possess a chemical potential given by

$$d\mu_j = 2RT \, d \log_e m_j \gamma \tag{11}$$

where γ is the activity coefficient and m_j is the molality (11, p. 328). Substituting in equation (8),

$$\omega = -\frac{2RT}{1000} \int_0^{mi} m_j \, d \log_e m_j \gamma \tag{12}$$

As the activity coefficients of NaCl in water are accurately known from e.m.f. and vapor-pressure studies, equation (12) will be used to calculate the osmotic potential of a 1.859 molal solution of NaCl at 25°C. and atmospheric pressure. The integral in the above equation has been found (18) by numerical integration to be equal to 1.815. The osmotic potential is therefore given by

$$\omega = \frac{-2RT}{1000} \times 1.815 = \frac{-2 \times 8.3136 \times 10^7 \times 298.18 \times 1.815}{1000}$$

$$= -90.0 \times 10^6 \text{ ergs/gram}$$

By the foregoing method it is possible to calculate the osmotic potential of any binary solution for which the activity coefficients are known. Consequently, because of the identity of ω and μ in aqueous solutions, "isopiestic" standards may be prepared from a great variety of aqueous solutions for use in static vapor-pressure measurements.

Whenever, as in the preceding examples, the chemical potentials of the solutes are known as a function of the composition of the solution, precise calculation of the osmotic potential is possible. In an aqueous solution of electrolytes containing *several* ionic species the problem is complicated by the fact that each species influences the chemical potential of every other species because of interionic attractions, as in the case of NaCl. This makes integration of equation (8) difficult for the liquid phase of the soil, which generally contains a number of electrolytes. For dilute solutions a rough approximation may be made by neglecting the interionic attractions and using equation (10), letting $\sum_j m_j$ represent the sum of the molalities of all molecular and ionic species present.

Knowledge of the composition of the liquid phase of the soil depends upon some means for obtaining a sample of the "soil solution" for analysis. Because of the complications already mentioned, it is often simpler to determine the osmotic potential directly from vapor-pressure or cryoscopic measurements of the extracted solution. The equations just presented have been found of value, however, for special purposes in moisture studies.

CALCULATION OF THE MOISTURE POTENTIAL FROM TENSIOMETER DATA

When a porous vessel containing water is inserted in moist soil, exchange of water between the two may be prevented by carefully regulating the pressure P^β of the water in the vessel; P^β is then found to be lower than the pressure P^α imposed upon the soil by the gaseous phase, although the two are equal if the soil is flooded with water. The significance of this observation, interpreted in the light of Buckingham's earlier studies (2), was first pointed out by Gardner, et al. (6). By means of baked porous-clay instruments, commonly called "tensiometers," many measurements of the kind described above have since been made for the purpose of determining the energy with which the liquid phase is held in the soil.

It will be recalled that the moisture potential may be calculated directly from vapor-pressure measurements and, as will be shown, from freezing-point measurements. For the purpose of correlating these with tensiometer measurements, it will be desirable to show how the moisture potential may be calculated from tensiometer data.

Suppose that a tensiometer containing an aqueous solution of the same composition as the liquid phase of the soil is inserted in the soil and equilibrium is established by suitably regulating the pressure. The condition for equilibrium is that the moisture potential μ^α in the soil be equal to the moisture potential μ^β in the tensiometer liquid. It follows from this that the equality of $d\mu^\alpha$ and $d\mu^\beta$ is also a condition for equilibrium (8, p. 88). The variation $d\mu^\beta$ is found from equation (7) to be

$$d\mu^\beta = v^\beta dP^\beta + d\omega^\beta \qquad (13)$$

The integral of this expression is

$$\mu^\beta = v^\beta(P^\beta - P^\alpha) + \omega^\beta \qquad (14)$$

where μ^β, ω^β, and $(P^\beta - P^\alpha)$ all approach zero at infinite dilution of the soil.

The tensiometer liquid, by hypothesis, has the same composition as the liquid phase of the soil; thus, in addition to the condition that $\mu^\alpha = \mu^\beta$, there are the supplementary conditions that $\omega^\alpha = \omega^\beta$ and $v^\alpha = v^\beta$. By making these substitutions in equation (14) it is found that

$$\mu^\alpha = v^\alpha(P^\beta - P^\alpha) + \omega^\alpha \qquad (15)$$

which gives the moisture potential μ^α of the soil in terms of the observed pressures, the partial specific volume[2] of water in the liquid phase, and the osmotic potential of the liquid phase.

If the tensiometer liquid were replaced by pure water, the pressure P^β should not be affected because the function of the tensiometer liquid in this equilibrium is merely to support the hydrostatic pressure. As solute diffusion is a slow process, equation (15) should apply to this "partial" equilibrium by reason of the slowness of approach to true equilibrium (11, p. 182). The latter type of

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[2] Approximately equal to 1 cc. per gram for dilute solutions.

equilibrium is more common in tensiometer studies than the hypothetical one through which equation (*15*) was derived.

The conclusion to be drawn is that the moisture potential, which may be calculated directly from vapor-pressure measurements, may also be calculated from tensiometer measurements by means of equation (*15*) if the osmotic potential and the partial specific volume of water in the liquid phase are known. It is obvious that this conclusion applies equally well to data obtained from the pressure-membrane and centrifugal techniques (13, 14), since these methods, like the tensiometer method, depend upon the establishment of pressure equilibria across "membranes" permeable to both solute and solvent. In a subsequent paper, moisture-potential values obtained from cryoscopic data will be compared with tensiometer data interpreted by equation (*15*).

THEORY OF THE CRYOSCOPIC METHOD

Schofield and Botelho da Costa (15, 16) were the first to use the cryoscopic, or freezing, method in determining the free energy of soil moisture. No derivation of their equation was given, though later (17) they stated their basic assumption that after freezing has occurred the ice exists in macroscopic crystals at atmospheric pressure. Upon this assumption the Schofield equation may be developed in a straightforward manner, as has been shown by Day (3). No hypothesis is necessary regarding the physical state of the water remaining unfrozen, but it must be assumed that after inception of freezing, equilibrium of moisture is rapidly attained. The experimental conditions may be arranged so that approximate thermal equilibrium is rapidly reached, and the amount of ice formed may be calculated.

The derivation of the Schofield equation depends upon the principle that at equilibrium the moisture potential of the ice must be equal to that of the soil. The moisture potential of ice at atmospheric pressure may be readily computed as a function of temperature, and therefore the moisture potential of the soil may be determined. The following thermodynamic cycle will be employed:

Begin with a large mass of moist soil, at its freezing temperature ($T°$ Kelvin) and at atmospheric pressure, with macroscopic crystals of ice scattered throughout the mass. Using a membrane permeable only to water, establish equilibrium between the soil at atmospheric pressure and pure water at a pressure P on the opposite side of the membrane.

1. Transfer a small mass δm of water across the membrane. 2. Restore δm to atmospheric pressure. 3. Elevate its temperature to the freezing point of water ($T_0°$ Kelvin). 4. Freeze. 5. Return δm to the original temperature. 6. Restore the ice to the soil; here it may melt reversibly because of the equilibrium which, by hypothesis, exists between ice and moist soil.

The change of free energy experienced by the mass δm in each step of the cycle will be equal to the change in moisture potential multiplied by δm, since differences of free energy depend only upon initial and final states. If the moisture potential μ at the start of each step is distinguished by a superscript representing the number of the step, the successive changes in free energy will be as follows:

1. $(\mu^2 - \mu^1)\delta m = 0$

2. $(\mu^3 - \mu^2)\delta m = -\mu^2\delta m = -\mu^1\delta m$

3. $(\mu^4 - \mu^3)\delta m = \delta m \int_T^{T_0} -s^w dT = -s^w(T_0 - T)\delta m$

4. $(\mu^5 - \mu^4)\delta m = 0$

5. $(\mu^6 - \mu^5)\delta m = \delta m \int_{T_0}^T -s^i\, dT = -s^i(T - T_0)\delta m$

6. $(\mu^1 - \mu^6)\delta m = 0$

where s^w and s^i represent the specific entropies[3] of liquid water and ice, respectively. By summing up all the terms on the left and equating to the sum of the final terms on the right, it is found that

$$\mu^1\delta m = -(s^w - s^i)(T_0 - T)\delta m \qquad (16)$$

The change in entropy during freezing (step 4) is equal to the heat absorbed ($L_f = -3.336 \times 10^9$ ergs per gram) divided by the temperature of the process ($T_0 = 273.18°K$); this quotient may be substituted for ($s^i - s^w$) in equation (16). Dividing through by δm, replacing ($T_0 - T$) by ΔT, and omitting the superscript, it is found that

$$\mu = \frac{L_f}{T_0}\Delta T \qquad (17)$$

which is equivalent to the form given by Schofield[4] (15).

COMPARISON OF THE CRYOSCOPIC TECHNIQUE WITH THE STATIC VAPOR-PRESSURE METHOD

The approximate validity of equation (17) for aqueous solutions has been thoroughly established (5). Experimental verification is needed, however, for systems in which uncertainty exists regarding the type of mechanism responsible for the depression of the moisture potential. For this reason, an effort has been made to check the cryoscopic technique with results obtained by the static vapor-pressure method.

The latter measurements were made by exposing samples of soil, initially wetted to their moisture equivalents, to the atmosphere over 0.600 M NaCl at 0°C. The freezing point depression of this solution was found to be 2.017°C., by interpolation in the International Critical Tables, volume 4, page 258. The corresponding moisture potential at 0°C. is -24.6×10^6 ergs per gram. The samples were exposed for 23 days in a desiccator evacuated to approximately 4 cm. of mercury. Dry air was slowly admitted and the moisture percentages

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[3] The variation of entropy with temperature is slight over the temperature ranges considered in this paper and therefore will be considered constant in the derivation.

[4] Unfortunately, a typographical error occurred in Schofield's original paper (15) but was later corrected (17). The meaning and algebraic sign of the quantity H in these two papers were never completely clarified.

were determined. The mean of two closely agreeing duplicates has been entered in table 1.

Freezing measurements were made on these soils by a thermoelectric method (1), which has been improved and which will be more fully discussed in a separate paper. The freezing points, determined for each soil over a wide range of moisture contents, were converted to moisture potential values by means of equation (17). The moisture contents were corrected for the amount of water removed from the liquid phase during ice formation.[5] The curves of moisture potential vs. corrected moisture content were then used for estimating the effective moisture content at a moisture potential of -24.6×10^6 ergs per gram.

Results from the two methods are given in table 1. From the last column it is shown that the cryoscopic method gives a systematically higher moisture content at equilibrium than does the vapor-pressure method. This is unfortunate, because the moisture potential is particularly sensitive, near the permanent wilting percentage, to small differences of moisture content.

TABLE 1

Comparison of the cryoscopic and the static vapor-pressure technique for soils at a moisture potential of -24.6×10^6 ergs per gram

SOIL NUMBER	MOISTURE EQUIVALENT	PERMANENT WILTING PERCENTAGE	EQUILIBRIUM MOISTURE PERCENTAGE		DIFFERENCE
			Cryoscopic method	Static vapor-pressure	
548	5.5	2.0	1.5	1.2	0.3
623	16.1	5.9	4.4	4.7	−0.3
607	16.2	6.1	6.0	5.0	1.0
616	26.9	12.8	12.7	11.1	1.6
604A	27.7	14.0	14.0	11.7	2.3
619A	31.2	20.5	19.7	18.2	1.5

Edlefsen and Anderson (5) have suggested that the freezing point of water in the immediate vicinity of the adsorptive surfaces of the soil will be affected by the hydrostatic pressure developed in these areas. According to the Clausius-Clapeyron equation, there is a maximum pressure above which ice cannot exist in equilibrium with water at a given temperature. It therefore seems plausible, as Edlefsen and Anderson have assumed, that the pressure exerts a controlling influence on the thickness of the layer of water remaining unfrozen. When ice crystals at atmospheric pressure are embedded in the soil, however, equation (17) must be satisfied at equilibrium and there can be only *one* temperature corresponding to any given moisture potential; hence the moisture potential is a controlling factor under these conditions, and the thickness of the layer of unfrozen water within the adsorption layer is an incidental factor.

According to the theory of capillarity there is a restriction on the maximum size of pore that can retain water at any given moisture potential, but there

[5] The magnitude of this correction was, on the average, about 1 per cent of the oven-dry weight of soil, i.e., about 1 per cent on the scale of moisture contents used.

is no corresponding restriction on the *minimum* size of pore. Consequently, means for estimating the relative amounts of water held by capillarity and by adsorptive forces are limited. In cryoscopic measurements the amount of heat evolved immediately after the inception of freezing makes it seem plausible that rather large masses of water, held in the form of "wedges" or filling some of the pores and unstable thermodynamically at the initial temperature, are suddenly converted to ice. The extreme difficulty experienced in attempting to freeze a sample of soil below its permanent wilting percentage indicates that ice does not readily form within the thin films of moisture surrounding the soil particles. With these points in mind there seems to be no reason to assume that the growth of ice crystals is restricted to the adsorptive areas; on the contrary there seems to be considerable reason to suppose that the areas of crystal growth are more extensive, and consequently subject to the normal pressure of the atmosphere.

The failure of dilatometer studies of biological tissues to give results consistent with thermodynamics has been interpreted by Kistler (10) to be due to freezing in isolated parts of the mass. If a similar interpretation is applied to freezing measurements of soils, it is seen that irregular freezing would excessively reduce the moisture content locally, and the calculated correction to the moisture content would be too small. This seems to be the most likely explanation of the disagreement found in table 1.

It should not be concluded that freezing-point studies should be abandoned; on the contrary, interesting information has been gained through their use. It is believed that the difficulties encountered are largely those of technique and may be overcome by experimental means. On the other hand, these defects must be corrected before the cryoscopic method will give results entirely consistent with thermodynamics.

SUMMARY

The moisture potential has been defined as the chemical potential of water in ergs per gram. It is identical with the partial molal free energy of water in all respects except for the unit of mass employed.

In accordance with previous terminology the moisture potential of an aqueous solution has been called the "osmotic potential." A general relationship between composition and osmotic potential has been presented and methods of calculation have been discussed.

It has been shown that the moisture potential of a soil may be calculated from tensiometric, centrifugal, or pressure-membrane methods, provided the osmotic potential and the partial specific volume of water in the liquid phase are known. This relationship is important where it is desired to compare these types of data with vapor-pressure or freezing-point data.

The theory of the cryoscopic method has been developed and an equation similar to that of Schofield has been derived. A comparison of cryoscopic data with data from static vapor-pressure measurements has demonstrated that the freezing method must be further improved before results completely consistent with thermodynamics can be obtained. A possible explanation of the discrepan-

cies is that irregular freezing results in excessive withdrawal of water from the liquid phase in the localized areas in which ice crystals have formed.

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LOSS OF AMMONIA FROM AMMONIUM SULFATE APPLIED TO ALKALINE SOILS

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A recent study by Crowther[2] of the relative efficiency of calcium nitrate and of ammonium sulfate when applied to cotton in the Sudan Gezira showed that crop increases are consistently greater with the calcium nitrate. Several possible explanations were suggested for this difference in fertilizer behavior, among them that loss of gaseous ammonia may take place from ammonium sulfate.

A direct search has shown that the loss of ammonia from the sulfate is indeed very considerable. It is natural to ascribe this loss to the alkalinity of Gezira soil.[3] That some loss of ammonia must be expected has always been recognized, but how serious this loss can be under certain circumstances was not heretofore realized. The purpose of the present study was to compare certain other soils with Gezira soil in this respect.

EXPERIMENTAL METHOD

Known quantities of ammonium sulfate were added to thin layers of soil in wide-mouthed bottles. The stoppers of the bottles were fitted with glass tubes so that a stream of air could be drawn over the surface of the moist soil. The air was then passed through a dilute solution of H_2SO_4 of known strength. The ammonia lost by the soil was estimated in this dilute acid at suitable intervals by means of Nessler's reagent, checked by titration. The loss of ammonia from the soils was found to be closely related to the water loss, which was determined by weighing the bottles before and after aspiration, using for the purpose an Avery semi-self-indicating balance reading to 0.1 gm.

In the main, 0.15 to 0.30 millimol of ammonium sulfate was applied to 20 gm. of soil. To estimate how such applications compare with field practice requires a knowledge of the distribution of the ammonium sulfate in depth, and this depends on the water added with or after the sulfate. In the field, broadcast applications ranging up to 550 pounds of sulfate of ammonia per acre have been made. In the vessels used in these experiments 0.006 m.e. corresponds to an application of 1 pound per acre on a simple area basis of comparison. Thus the experimental applications range from 25 to 50 pounds per acre on this basis. Experimentally, however, the ammonium sulfate is applied in solution, and field applications are made during the rainy season; therefore, an adjustment

has to be made for distribution in depth. In the field on Gezira soil, which cracks severely, some sulfate is washed directly to deeper levels, but the remainder is held in the surface inch, even with heavy applications of water. In the experimental bottles the soil layer (with 20 gm.) is about one-fifth of an inch thick. As far as the immediate surface is concerned, the experimental applications therefore are equivalent to heavier field applications than 25 to 50 pounds per acre. A precise comparison cannot be attempted, but it is clear that the experimental applications are within the range of field applications.

LOSSES FROM DIFFERENT SOILS

For the comparison of losses from soils of different alkalinity, the following soils were selected:

SOIL	pH	LOCATION
Gezira	9.3	Sudan Gezira
Gash	8.6	Kassala
Berber	10.5	Northern Sudan
Maridi	7.0	Southern Sudan

With the exception of the Berber soil, these are important cultivated Sudan soils.

TABLE 1

Losses of ammonia from ammonium sulfate applied to soils

SOIL	NH₃ LOSS	
	millimols	*per cent*
Gezira	0.02	13
Gash	0.02	13
Berber	0.13	87
Maridi	0	0

Twenty grams of each soil (air-dry), was treated with 0.15 millimol of ammonium sulfate applied in 10 cc. of water. A slow stream of air was drawn over the samples, and daily estimations of the ammonia loss were made. When loss of moisture ceased, 10 cc. of water was added to each sample and drying was continued until 20 gm. of water had been lost in all, leaving the samples approximately in an air-dry state. The total amounts of ammonia lost during this period are shown in table 1.

The procedure was then repeated, except that the initial quantity of water was 15 cc. and the subsequent application 5 cc.

Figure 1 shows both sets of results for the three soils that lost measurable quantities of ammonia, the progressive loss of ammonia being plotted against the corresponding water loss. The curves for the Berber soil differ markedly from

those for the other two soils.   Examination of the results for the Gezira and Gash soils leads to an explanation of this difference, and these two soils therefore are considered separately.

It will be observed that Gezira and Gash soils lost the same amount of ammonia within the limits of experimental error.   The curves show that loss of ammonia is related to the loss of water, and there is no sharp break in the curves
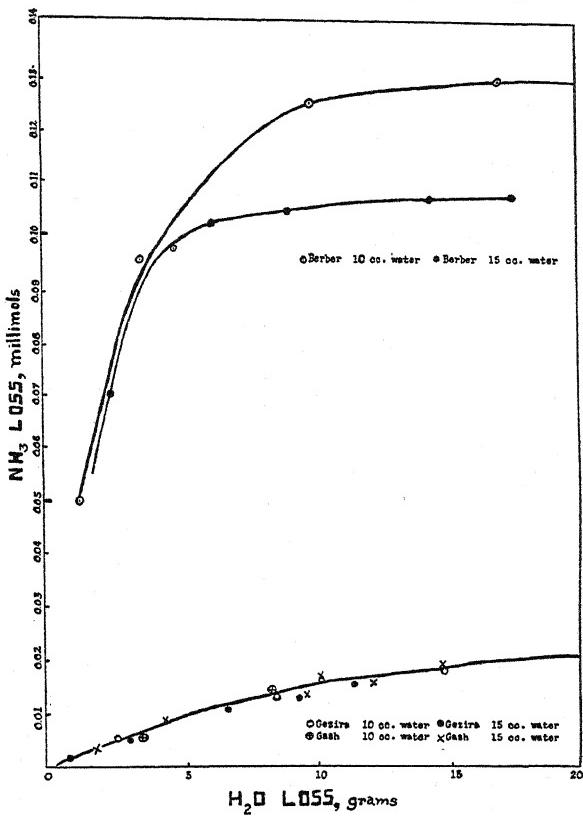
FIG. 1. LOSSES OF AMMONIA IN RELATION TO LOSSES OF WATER
FROM BERBER, GEZIRA, AND GASH SOILS

at the point where additional water was added, i.e., at 10 cc. and at 15 cc. in the two different treatments.

This is further illustrated by the results of a similar experiment with Gezira standard soil (a surface soil that had been stored for several years in sealed containers) continued over a longer period.   The first procedure, involving treatment with the more concentrated solution of ammonium sulfate and periodic additions of 10 cc. of water, was followed.   Table 2 shows the progressive daily totals of ammonia loss and of water loss.   Of the 0.15 millimol of ammonia added, 28 per cent was lost by the end of the experiment.

LOSSES WITH DIFFERENT APPLICATIONS OF AMMONIUM SULFATE

During the same period a similar experiment was in progress with two other treatments, 0.06 and 0.3 millimol ammonium sulfate. The results are shown in table 3. These figures, together with those in table 2, show that the actual

TABLE 2

Progressive daily totals of ammonia loss and of water loss from Gezira standard soil treated with ammonium sulfate*

AMMONIA LOSS	WATER LOSS
millimols	*gm.*
0.0055	1.9
0.0100	6.1
0.0115	7.5†
0.0120	8.1
0.0155	12.4
0.0190	15.9
0.0195	17.7†
0.0235	24.4
0.0245	27.4
0.0245	27.5†
0.0280	29.2
0.0320	31.2
0.0340	32.7
0.0365	35.9
0.0365	37.4†
0.0395	40.8
0.0410	43.3
0.0420	45.4
0.0420	47.1†

* Ammonium sulfate added to 20 gm. of soil, 0.15 millimol.
† 10 gm. of water added to replace that lost by evaporation.

TABLE 3

Losses from Gezira standard soil with different applications of ammonium sulfate

$(NH_4)_2SO_4$ ADDED.....................................*millimols*	0.06	0.30
Water added.................................*cc.*	10	10
Total losses		
Water.................................*gm.*	49.7	48.8
Ammonia.........................*millimols*	0.023	0.084
Ammonia.........................*per cent*	39	28

loss of ammonia is markedly influenced by the amount of the fertilizer applied, and that in each case it is of very considerable magnitude.

To determine whether Gezia standard soil is strictly comparable with field soil, a direct comparison was made. The procedure previously outlined was

followed with the two samples, each of which was treated with 0.15 millimol of ammonium sulfate in 10 cc. of water. For some reason, probably varying rates of aspiration, the samples dried at different rates, with the result that they are not directly comparable with complete propriety. The following results were obtained:

		Standard soil	Field soil
Total NH₃ loss.................................*millimols*		0.05	0.04
Total water loss...*gm.*		83	68

The daily readings do not indicate that continued evaporation from the field sample would have increased the ammonia loss to the level of that of the Gezira standard soil. It is clear, however, that the field soil shows a very considerable loss of ammonia, amounting in this case to 27 per cent of the quantity applied.

MECHANISM OF THE REACTION

The basic factors revealed by the experiments are the paramount influence of the total quantity of ammonium salt present, and the close relationship between the loss of ammonia and the loss of water. The moisture content itself does not appear to have an important effect. Loss of ammonia ceases when there is no loss of moisture.

The soil solution in these experiments is alkaline and contains small concentrations of ammonium ions which are in equilibrium with ammonium ions in the base-exchange complex. In such a solution the equilibrium $NH_4^+ + OH^- \rightleftharpoons H_2O + NH_3$ is presumably established, the ammonia and the water have their own partial pressures and evaporate together in proportions governed by their relative molar concentrations. The reversible reaction between the ammonium ion and the base-exchangeable complex tends, however, to maintain constant the concentration of ammonium ion. The soil solution, in this way, is buffered to some extent against changes in its ammonium-ion concentration. The soil is also buffered with respect to OH^- concentration. The equilibrium between molecular ammonia and the ammonium and hydroxyl ions therefore is maintained constant.

If this interpretation is correct it would be expected that the ratio of NH_3 loss to H_2O loss would remain substantially constant.

The curve in figure 1 for Gezira and Gash soils shows that this is approximately the case. The ratio NH_3 loss to water loss falls off slowly, indicating that the reserve of ammonium ions in the base-exchange complex is sufficient only partly to maintain the ammonia concentration in solution. Such a mechanism as this is able to explain the small influence exerted on the reaction by the moisture concentration, for the base-exchange equilibrium is not influenced by the soil-water ratio as a first-order effect. Naturally, increase in the total quantity of ammonium salt present has a direct effect on the concentration in the soil solution.

It is of interest to determine the concentration of ammonia in the liquid in equilibrium with the soil under conditions such as the ones under review. The concentrations of ammonium sulfate employed in these experiments are much

lower than those commonly used in base-exchange studies. The use of only 10 cc. of solution with 20 gm. of soil makes it difficult to obtain a satisfactory estimate of the concentration in the soil solution. By filtering under reduced pressure with 0.15 millimol of ammonium sulfate in 10 cc. of water applied to 20 gm. of Gezira soil it has been found that the concentration of ammonia in the soil solution is about 0.0005 N. The order of this concentration has been checked by a determination using 0.30 millimol in 20 cc. of water with 20 gm. of soil, when a soil solution concentration of 0.0006 N was measured.

If, as evaporation goes on, this concentration is maintained, in accord with the mechanism outlined, it should be possible to compare the ratios of ammonia and water losses with those obtained when dilute solutions of ammonium sulfate are evaporated in alkaline solutions. The pH of Gezira soil is 9.3, which corresponds to a OH^+ concentration conventionally equivalent to between 0.0001 N and 0.00001 N.

Direct measurements of the ratio of ammonia loss to water loss have been made by drawing a stream of air through a weighed solution of 0.001 N ammonium sulfate containing various amounts of sodium hydroxide. The ratios of ammonia lost (in cubic centimeters of 0.01 N ammonia) to water lost (in grams) were directly proportional to the concentration of the sodium hydroxide. The ratio measured was 0.2 when the hydroxide concentration was 0.0003 N. Gezira soil in figure 1 gives a mean ratio of ammonia loss to water loss of 0.1 over the whole range, using the same units as above for the ratio. Since here the ammonium concentration in the soil solution was of the order 0.0005 N, the agreement is fairly satisfactory.

This suggests that the behavior of soils with respect to this loss of ammonia depends primarily on their pH and on their base-exchange relationships with the ammonium ion.

The comparable data given in figure 1 for Gash and Gezira soils show that, though the pH of the former is lower than that of the latter, the ammonia losses are the same within the limits of experimental error. This suggests the advisability of examining the two soils in their base-exchange relationships with ammonium sulfate. This was done by adding 20 gm. of each soil to 20 cc. of 0.015 N ammonium sulfate solution, and estimating the ammonia in the filtrates. Results for Maridi and Berber samples are also given:

SOIL	CONC. OF NH₃ IN FILTRATE	TOTAL NH₃ IN 20 CC.
	N	*millimols*
Gezira..	0.0006	0.012
Gash...	0.0013	0.026
Berber...	0.0060	0.120
Maridi...	0.0017	0.034

These results show that under the present conditions, where small additions of ammonium sulfate are made, the soil solution in Gash soil contains a higher concentration of ammonia than does Gezira soil. This offers a partial explana-

tion of the fact that, despite its high pH, the Gezira soil does not have a greater ammonia loss than the Gash soil.

It will be noticed that the concentration of ammonia in the filtrate for the Berber soil is very much higher than those for the Gezira and Gash soils. With the Gash soil, for example, more than 90 per cent of the added ammonium is held in the base-exchange complex, whereas this figure for the Berber soil is only 60 per cent. The mechanism suggested for the loss of ammonia from Gezira and Gash soils would not therefore be so effective with the Berber soil. In this case the concentration of ammonia in the soil solution is large, and consequently the initial rate of loss of ammonia is large, whereas the available reserve in the base-exchange complex is much smaller than with the other two soils and is insufficient to maintain the ammonia concentration constant for any considerable period.

The curves in figure 1 for Berber soil show that loss of ammonia virtually ceases after the loss of 15 cc. of water. From the amounts applied and from the total loss at this point, however, it can be shown that a concentration of ammonia remains which is sufficient to give further losses capable of measurement, if some other factor were not operative. Direct estimations of the nitrate formation were made, and as a result it was possible to show that sufficiently large amounts of nitrate were formed during the experiments to account for 80 per cent of the missing ammonia.

DISCUSSION

There would appear to be no doubt that the loss of ammonia from ammonium sulfate on alkaline soils found under experimental conditions would also occur in field practice where the ammonium sulfate is applied to the surface. Many alkaline soils, however, are subject to deep cracking under arid conditions. Where this happens, rain falling after the broadcasting of the fertilizer may result in the mass movement of the resulting solution down cracks, to depths where loss of the type described in this paper would be small.

In this connection it may be mentioned that Crowther found that buried ammonium sulfate was much more efficient than the broadcast fertilizer. It seems probable that some of the difference may be due to decreased loss of ammonia when the fertilizer is buried.

In Gezira and Gash soils, ammonium sulfate that does not find its way down cracks is held firmly in the upper layer, where it is exposed to repeated wetting and drying until nitrification takes place. By leaching experiments it has been possible to show that 80 per cent of a small application of ammonium sulfate is recoverable from the surface inch of Gezira soil after an equivalent of 8 inches of water has been applied. Nitrification in this soil is slow enough to allow considerable loss of ammonia to take place. Loss of ammonia from the Berber soil is quickly stopped by nitrification, but not before 60 to 70 per cent of the applied ammonia has been lost under experimental conditions.

It seemed just possible that some of the measured loss of ammonia might be due to denitrifying organisms. A search was made for loss of ammonia when calcium nitrate was applied to Gezira soil. The results were negative; experi-

mental arrangements were such that a loss of less than 1 per cent daily would have been detected. It is interesting to note that moist Gezira soil, without added ammonium sulfate, loses only a trace of ammonia on drying. Yet a conventional estimation by distilling the soil with dilute sodium carbonate yields a considerable quantity of ammonia, of the order of 0.08 millimol per 20 gm. The loss of 10 gm. of water, obtained by the method of drawing air over the moist soil, was associated with the loss of less than 0.001 millimol per 20 gm. In a parallel experiment in which 20 gm. of Gezira soil was treated with 0.025 millimol of ammonia, 0.0045 millimol of ammonia was lost with 10 gm. of water. These results seem to indicate that this alkaline Gezira soil does not, when air-dried for a long time, contain any appreciable quantity of nitrogen as replaceable ammonium radical in the base-exchange complex. If the results of this work are of general application, this is probably true of other alkaline soils, in which case the absence of replaceable ammonium would possibly have an effect on the microbiological status of such soils.

In the extremely alkaline Berber soil, which loses great quantities of ammonia from ammonium sulfate, it may be observed that such a loss would be much reduced in practice by the very fact that the soil solution contains such a high concentration of ammonia, for this means that much of the applied fertilizer would be rapidly removed by rain or irrigation to deeper soil layers. In comparison with the Gezira and Gash soils, this removal would be increased by virtue of the much smaller capacity of the Berber soil to hold water against gravity. It is therefore very doubtful whether the field loss would be nearly so great as under the present experimental conditions.

The work reported has been briefly extended in the direction of higher applications of the ammonium salt up to 1.0 millimol per 20 gm. of Gezira soil with 15 cc. of water. This corresponds to a rate of 170 pounds per acre. Of this application about 12 per cent was lost while the 15 cc. of water evaporated. Reference to figure 1 shows that about 15 per cent of the lighter 0.15-millimol application was lost with the same quantity of water. The curve ammonia loss against water loss for this higher rate of application shows a considerable falling off in the rate of ammonia loss as evaporation proceeds, suggesting that the base-exchange complex is unable to replenish the ammonium concentration in the soil solution sufficiently rapidly to replace the loss of ammonia. It must be recognized that the rate of loss of ammonia may be limited in some circumstances by the rate of diffusion through the soil, and not by the rate at which the base-exchange complex can give up the ammonium ion to the solution. Further, it it has been possible to show that the percentage of added ammonia held by the exchangeable-base complex diminishes rapidly as the amount of ammonia added increases. This means that with heavier applications of ammonium sulfate the capacity of the exchange complex to maintain the solution concentration constant is diminished as compared with light applications.

It may be noted that Crowther found from his statistical analysis of crop yields that the apparent loss of ammonia was the same irrespective of the amount of fertilizer applied. That is to say, at low rates of application calcium nitrate

showed a pronounced superiority over ammonium sulfate, whereas at high rates of application the increased yields with both types of fertilizer were similar.

He deduced that the loss of 20 pounds of nitrogen with all rates of sulfate application would account for the differences between the two types of fertilizer.

The experiments reported in this paper show, however, that the loss of ammonia increases rapidly with increased rate of application, and there would seem to be no valid reason why this should not also be the case in the field. If this is so, the difference in efficiency of calcium nitrate and ammonium sulfate does not appear to be directly explicable as due simply to the loss of ammonia from the ammonium sulfate.

SUMMARY

It has been found that gaseous ammonia is lost in considerable quantities when ammonium sulfate is applied to certain alkaline Sudan soils. The loss takes place over long periods from the moist soil, at a rate greatly influenced by the rate of application of the fertilizer and little influenced by the moisture content except when this approaches air-dry levels.

A mechanism for the loss is suggested, according to which the base-exchange equilibrium in the soil tends to maintain the concentration of ammonia in the soil solution at a constant level, whereas the normal buffered state of the soil solution maintains constant the hydroxyl-ion concentration. Under these circumstances the ammonia is lost as from a dilute solution, at a constant rate proportional to the ammonia concentration in the soil solution. This loss will continue (if the soil is kept moist) for a long or short period, depending on the reserves of ammonium ions in the base-exchange complex. If the exchange capacity is low, the rate of loss of ammonia is not maintained constant and is comparable with that from a dilute solution the ammonia content of which declines progressively as evaporation proceeds.

It is considered probable that commercially important losses of ammonia occur in the field when ammonium sulfate is broadcast on alkaline soil.

CARBON-NITROGEN RATIOS IN ORGANIC FERTILIZER MATERIALS IN RELATION TO THE AVAILABILITY OF THEIR NITROGEN[1]

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The nitrogen of fertilizer materials of animal or vegetable origin is, for the greater part, combined in complex proteinaceous compounds many of which are largely insoluble in water. If such nitrogen is to be converted to soluble forms that are utilizable by plants, the parent materials must be subjected to the agencies of decomposition in the soil.

The use of organic fertilizer materials has suffered a relative decline since the beginning of large-scale production of soluble inorganic nitrogen salts. Their cost has also risen as the better materials have gone more and more into stock feed, forcing the fertilizer mixer to compete with the feed manufacturer, who can generally pay a better price.

Despite this, a demand for natural organic forms of nitrogen persists. This is especially true in regions of high rainfall and sandy soils, and in connection with the production of crops of high acre value. To fill this demand, organic materials that are unfit for feeds are used either in their natural state or after pretreatment with steam or acid to make their nitrogen more available to plants. In some cases low-nitrogen organic materials are used in mixed fertilizers as conditioners rather than for the nitrogen they contain.

The availability to plants of the nitrogen of organic fertilizer materials, known to the trade as organic ammoniates, varies greatly. In order to evaluate such nitrogen, control chemists, using vegetative tests as reference points (2), have subjected the water-insoluble portions of such ammoniates to various chemical treatments, among which the neutral and alkaline permanganate methods are the best known. Other workers (4) have employed ammonification and nitrification procedures. More recently, soil chemists and bacteriologists have made use of the principle of the carbon-nitrogen ratio to explain the differences in the availability of the nitrogen in soil organic matter (3, 6). It seemed worth while, therefore, to consider this principle for possible application in evaluating the nitrogen of organic ammoniates as well.

EXPERIMENTAL PROCEDURES

Preparation and analysis of materials

Thirty-four organic materials, most of which could properly be classed as ammoniates, were collected and prepared for use in this study. Subsamples were taken from the air-dry materials and ground to pass a 1-mm. sieve, either an iron mortar or a Wiley mill being used.

Since it was desired to conduct much of the work on the water-insoluble fraction of these materials, a method was devised to free 100-gm. portions of them of soluble matter with a minimum expenditure of time. That amount of each material, moistened with alcohol, was stirred with 1500 ml. of distilled water, which was then decanted through a Sharples supercentrifuge. This process was repeated three times. The residue, including the rotor contents, was transferred to a Büchner funnel, given a final washing, and dried at 50°C. After this treatment, 15 of the 32 materials so washed averaged more than 98 per cent, 12 between 95 and 98 per cent, and none less than 89.4 per cent insoluble matter. The materials and their analyses are listed in table 1.

Vegetative test

For greenhouse studies of the availability of the nitrogen of these organic materials, 2-gallon pots, each containing 18 pounds of the A_p horizon of Collington sandy loam, were used. After a standard treatment of dolomitic limestone, superphosphate, and muriate of potash, the various materials were added to and mixed with the entire volume of soil in each pot. The rate of fertilization was 1600 pounds of a 5-10-10 mixture per 2,000,000 pounds of soil, supplying 0.3266 gm. of nitrogen per pot. The soil was seeded to Sudan grass which, thinned to 12 plants per pot, was grown for 60 days from mid-April, 1942. Green and dry weights and nitrogen content were obtained on the tops, and dry weight and nitrogen content on the roots.

Nitrification method

The method adopted to test the rate of nitrification of the nitrogen contained in the various materials consisted of mixing the amount of each material that would supply 20 mgm. of nitrogen with a 100-gm. portion of Collington sandy loam, placing the mixture in a 500-ml. Erlenmeyer flask, and incubating it at 28°C. under optimum moisture conditions. Preliminary tests having shown that the addition of potassium and phosphorus, as K_2HPO_4, to the cultures had little effect upon the results obtained, only $CaCO_3$ (0.2 gm. per flask) was added to the soil as a supplement to the organic material. Nitrates were determined by the phenyldisulfonic acid method at the end of the incubation periods.

The procedure yielded reproducible results. For example, the amounts of added nitrogen recovered as nitrate from unwashed dried blood, after 20 days' incubation, varied only between 57 and 62 per cent in six experiments conducted at various intervals over a period of 9 months. The variation in recovery of nitrate after 40 days varied only between 63 and 69 per cent in seven similar tests. Correspondingly good reproducibility was obtained with other materials.

TABLE 1
Nitrogen and insoluble-matter content of unwashed and washed organic materials

MATERIAL	UNWASHED				WASHED
	Total nitrogen	Water-insoluble nitrogen		Water-insoluble matter	Total nitrogen
		Of total weight	Of total nitrogen		
	per cent	per cent	per cent	per cent	per cent
Seed meals:					
Soybean meal	7.60	6.40	84.2	62.4	10.30
Cottonseed meal	7.24	6.73	93.0	76.5	8.70
Special soybean meal*	7.69	2.53	32.9	35.1	6.43
Castor pomace	5.03	4.67	92.8	86.1	5.12
Cocoa meal	2.98	1.91	64.1	69.2	2.95
Ground cocoa cake	3.06	2.29	74.8	87.1	2.85
Plant materials:					
Alfalfa hay	2.82	1.48	52.5	69.9	2.19
Tobacco stems	1.00	0.53	53.0	46.0	0.88
Peanut hull meal	1.24	0.98	79.0	86.5	0.89
Wheat straw	0.308	0.190	61.7	90.1	0.235
Process tankages:					
Hynite	9.57	8.21	85.8	80.4	10.07
Processed tankage	9.76	7.88	80.7	80.4	9.78
Agrinite	8.52	7.08	83.1	74.3	9.01
Smirow	7.01	6.60	94.2	82.2	7.92
Animal products:					
Hoof meal	14.28	8.67	60.7	56.9	14.48
Bone meal	4.16	4.15	99.8	93.2	4.39
Dried blood	13.83	13.49	97.5	91.2	14.66
Dry fish scrap	9.28	8.22	88.6	83.7	9.83
Animal tankage	8.83	5.65	64.0	65.8	7.93
Acid fish scrap	8.54	5.82	68.1	66.5	8.43
Manures:					
Peruvian guano	13.95	6.13	43.9	55.5	14.40
Bovung	2.01	1.40	69.7	80.6	1.76
Horse manure	1.45	1.16	80.0	80.1	1.32
Chicken manure	2.25	0.74	32.9	86.0	1.02
Sewage products:					
Milorganite	5.66	5.07	89.6	88.0	6.04
Nitroganic tankage	5.93	5.72	96.5	94.3	6.00
Sewage sludge	1.78	1.59	89.3	88.5	1.82
Plastics:					
Beetle molded-scrap†	19.76	19.42	98.3	97.5	20.10
Beetle scrap dust†	19.02	13.66	71.8	70.1	16.00
Ford molded-scrap‡	2.12	....	....	....	....
Ford molding powder‡	2.08	....	....	....	....
Miscellaneous:					
Cocoa tankage	2.52	1.98	78.6	75.9	2.51
Garbage tankage	2.66	2.49	93.6	80.4	2.80
Manito humus	2.48	2.48	100.0	84.4	2.71

EXPERIMENTAL RESULTS

Vegetative and nitrification experiments

The average recovery of added nitrogen in the tops and roots of Sudan grass when grown on soil to which the several organics[3], urea, and unwashed dried blood had been applied are listed in table 2. Comparison of the nitrogen recoveries by the vegetative test with those obtained from the same materials by the nitrification procedure, shows that the values with the two methods agree rather closely. Negative values resulted in the nitrification test when materials were added whose composition was such that all the nitrogen released by the organic material, as well as some or all of that in the substrate, was utilized by the soil microorganisms. This negative scale was made possible by the fact that a considerable amount of nitrate nitrogen was produced in check soil cultures to which no nitrogen carrier had been added. An analogous situation, in conjunction with the vegetative test, also resulted in negative nitrogen-recovery values.

Availability ratings greater than 50 per cent were found for the insoluble nitrogen of soybean meal, cottonseed meal, castor pomace, hoof meal, dried blood, dry fish scrap, and Peruvian guano, by both the vegetative and the nitrification procedures. The nitrogen of the special soybean meal and acid fish scrap was 50 per cent or more available by the 40-day nitrification test (compare with table 5) but not by the 60-day vegetative test. In contrast, more than 50 per cent of the nitrogen of Milorganite became available by the 60-day vegetative test but not by the 40-day nitrification test. The insoluble nitrogen of Peruvian guano showed the highest availability of any of the washed organics, 67 per cent of its nitrogen being converted to nitrate in 20 days, and 67.8 per cent being recovered in the vegetative test. The corresponding percentages for urea were 87 and 87.9 for the nitrification and vegetative tests, respectively.

Of the materials that contained more than 3 per cent nitrogen, the process tankages rated among the lowest in nitrogen availability, ranging between 12.9 and 24.1 per cent by the vegetative test and between 12 and 33 per cent by the nitrification procedure. The insoluble nitrogen of bone meal showed even lower availability. Acid fish scrap rated considerably higher by the nitrification test than by the vegetative method. The insoluble nitrogen of Beetle scrap dust, a urea-formaldehyde resin containing a quantity of molding powder, showed fair availability, whereas that of the scrap molded material, which had been subjected to heat treatment during the molding process, gave availability values close to zero. With these exceptions, washed organics containing 3 per cent or more nitrogen rated comparatively high, whereas those containing lesser amounts ranked low.

The A.O.A.C. alkaline and neutral permanganate numbers for the organics are also given in table 2. A satisfactory source of nitrogen should rate higher than 50 by the alkaline and higher than 80 by the neutral permanganate method,

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[3] Throughout this paper, when unspecified as to whether the organics are washed or unwashed, reference is to the washed materials.

TABLE 2

Carbon-nitrogen ratios and nitrogen availability ratings of various organic materials

MATERIAL	WASHED					UNWASHED	
		Permanganate activities		Vegetative test (Sudan grass)	Nitrification test	Nitrification test	
	C–N ratio	Alkaline method	Neutral method	Added nitrogen recovered in tops and roots	Added nitrogen converted to nitrate	Added nitrogen converted to nitrate	
					20 days	20 days	40 days
				per cent	*per cent*	*per cent*	*per cent*
Seed meals:							
Soybean meal	4.70	70.1	92.2	59.0	58	61	65
Cottonseed meal	5.40	66.9	82.7	53.6	50	49	54
Special soybean meal	7.05	49.6	73.9	43.9	50	61	66
Castor pomace	9.36	63.0	87.9	51.7	55	60	67
Cocoa meal	14.7	28.8	37.1	....	−1	14	22
Ground cocoa cake	19.0	33.2	51.5	−25.2	−14	−15	−5
Plant materials:							
Alfalfa hay	20.8	28.4	68.9	0.8	4	24	32
Tobacco stems	28.9	19.8	65.4	−25.3	−14	−14	5
Peanut hull meal	53.5	25.9	42.6	−2.6	−1	15	15
Wheat straw	197.0	....	....	....	−16	−16	−15
Process tankages:							
Hynite	4.87	73.2	80.9	24.1	24	31	37
Processed tankage	5.17	69.8	81.6	14.7	21	31	35
Agrinite	5.24	68.6	78.8	13.2	18	27	31
Smirow	6.30	64.2	71.8	12.9	13	17	18
Animal products:							
Hoof meal	3.31	77.1	93.2	50.1	57	65	68
Bone meal	3.46	81.9	39.9	8.8	6	7	10
Dried blood	3.51	81.1	87.9	56.3*	51	60	66
Dry fish scrap	4.42	72.8	86.0	50.1	51	59	63
Animal tankage	5.25	67.1	70.7	29.7	26	37	45
Acid fish scrap	5.28	68.0	87.9	22.0	33	56	61
Manures:							
Peruvian guano	1.28	41.3	96.7	67.8	67	80	77
Bovung	24.4	27.9	47.1	−15.6	−10	0	7
Horse manure	32.7	28.8	51.6	....	−19	−19	−16
Chicken manure	36.4	38.8	59.9	....	−19	22	30
Sewage products:							
Milorganite	5.98	63.4	75.2	50.5	44	48	53
Nitroganic tankage	6.20	65.1	83.7	37.2	41	44	47
Sewage sludge	13.7	51.1	65.4	8.4	8	11	16
Plastics:							
Beetle molded scrap	1.83	48.0	21.2	−2.4	1	1	1
Beetle scrap dust	2.35	67.5	79.7	37.2	20	23	30
Ford molded scrap	....	....	....	....	....	−5	−3
Ford molding powder	....	....	....	....	....	−3	−9

* Added nitrogen recovered from Sudan grass fertilized with unwashed dried blood was

TABLE 2—*Concluded*

MATERIAL		WASHED					UNWASHED	
	C-N Ratio	Permanganate activities		Vegatative test (Sudan grass)	Nitrification test	Nitrification test		
		Alkaline method	Neutral method	Added nitrogen recovered in tops and roots	Added nitrogen converted to nitrate	Added nitrogen converted to nitrate		
					20 days	20 days	40 days
				per cent	per cent	per cent	per cent
Miscellaneous:							
Cocoa tankage................	13.3	30.4	53.8	−6.9	−7	−2	13
Garbage tankage..............	13.4	30.6	51.1	−10.0	0	−6	−3
Manito humus................	13.7	44.4	40.9	−5.3	3	3	4
Standard material:							
Urea..........................	....	....	....	87.9	....	87	88

but only a failure in both tests can condemn the insoluble nitrogen of an organic ammoniate. Some discrepancies exist between these values and the actual availability data by the vegetative and nitrification methods. None of the decidedly inferior materials received a "passing" rating by the neutral method, but this method was poor in distinguishing between substances of good and those of intermediate availability. The special soybean meal is rated too low by both permanganate methods. Process tankages, animal tankage, sewage sludge, Beetle scrap dust, and bone meal are all rated too high by the alkaline method. Peruvian guano has high nitrogen availability, and rates satisfactorily by the neutral method, but its alkaline permanganate number is much too low. This fact has been noted by previous workers, and has been attributed to the presence of uric acid in the guano (2). Uric acid has a low alkaline permanganate number, yet its nitrogen is highly available to plants.

Nitrification of washed and unwashed organics

The nitrification values of the nitrogen of the unwashed organics may be compared with the corresponding values for the washed materials in table 2. Several unwashed organics containing less than 3 per cent nitrogen, unlike their washed counterparts, gave nitrification values bordering on the satisfactory. The nitrogen of unwashed chicken manure nitrified readily, whereas that of its water-insoluble portion did not. A similar tendency was observed with peanut hull meal, tobacco stems, Bovung, alfalfa hay, and cocoa meal. Ground cocoa cake, wheat straw, and horse manure, both washed and unwashed, proved to be very poor nitrogen sources, the net effect of their decomposition being the tying up not only of all their own nitrogen but of much of the nitrate in the substrate as well.

Of the materials containing more than 3 per cent nitrogen, the differences

between the nitrification of the nitrogen of the unwashed and that of the washed materials, in most cases, were not large. The greatest relative differences occurred with acid fish scrap, animal tankage, and the various process tankages. With these products, the nitrogen of the unwashed materials nitrified better than did that of the washed materials, implying that soluble nitrogen of high availability was lost in the washing process.

Nitrification as related to C–N ratio

It is a well-known fact that when a large amount of easily decomposable high-carbon organic matter is present in the soil, the microorganisms will feed on this material and, in so doing, will themselves appropriate the nitrogen which it contains, thus limiting, or entirely preventing, the accumulation of nitrates and, in extreme cases, tying up any nitrate in the substrate as well. As the

TABLE 3

Nitrification of mixtures of carbonaceous materials and sulfate of ammonia

CARBON SOURCE	CARBON CONTENT	C–N RATIO OF MIXTURE	ADDED NITROGEN CONVERTED TO NITRATE		
			20 days	40 days	60 days
	per cent		*per cent*	*per cent*	*per cent*
Lignin..................	57.2	20:1	86	85	86
Cornstarch..............	39.0	20:1	49	56	54
Dextrose................	35.8	20:1	49	52	50
Cottonseed oil...........	76.5	20:1	39	45	49
Cellulose................	42.0	5:1	77	76	77
Cellulose................	42.0	10:1	65	66	66
Cellulose................	42.0	20:1	41	45	49
Cellulose................	42.0	40:1	−2	7	21
Cellulose................	42.0	80:1	−19	−20	−18
No carbon added.........	....	....	91	83	85

decomposition process continues, however, the C–N ratios narrow and nitrate nitrogen accumulates. As a general rule, therefore, the wider the C–N ratio of a substance, the less immediately available to plants one would expect its nitrogen to be.

Inasmuch as carbon compounds differ in the ease with which they can be utilized by microorganisms, certain sources of carbon are more effective than others in depressing nitrification (6). To illustrate this point, synthetic mixtures containing varying C–N ratios were prepared and put through the nitrification procedure, ammonium sulfate being used as a source of nitrogen, and dextrose, cornstarch, cellulose, cottonseed oil, and lignin as sources of carbon. The data are presented in table 3.

At C–N ratios of 20 to 1, lignin does not depress nitrification; but cornstarch, dextrose, cellulose, and cottonseed oil exert considerable depressing effect, and in the order mentioned. The nitrification data on mixtures containing various

amounts of cellulose clearly illustrate the fact that, for easily decomposable sources of carbon, nitrate accumulation is inversely proportional to the C–N ratio.

Proximate analysis of washed organics

Since equivalent quantities of carbon from various sources were shown to have different effects on nitrogen availability, it was deemed desirable to know the proportions of certain of these carbon sources in the washed organics. Proximate

TABLE 4

Percentage proximate analyses of washed organic materials

FRACTION	COTTONSEED MEAL	SPECIAL SOYBEAN MEAL	CASTOR POMACE	COCOA MEAL	ALFALFA HAY	TOBACCO STEMS	PEANUT HULL MEAL	HYNITE TANKAGE	SMIROW	DRIED BLOOD	ACID FISH SCRAP	BOVUNG	HORSE MANURE	MILORGANITE	SEWAGE SLUDGE	GARBAGE TANKAGE	MANITO HUMUS
Ether-soluble	7.8	1.2	0.5	2.2	2.7	1.6	0.7	8.0	2.9	0.6	10.9	3.0	1.9	4.5	6.5	1.1	0.2
Alcohol-soluble	1.0	1.6	2.6	0.8	0.6	0.8	0.4	1.1	2.4	0.9	1.8	1.6	0.7	1.3	1.2	0.5	1.0
Cold water soluble	0.7	4.1	2.0	1.6	3.5	2.4	0.3	3.1	1.3	1.2	2.0	1.3	1.3	1.7	0.9	0.8	0.7
Hot water soluble	2.6	3.1	5.6	1.9	2.4	1.5	0.5	8.3	9.3	1.5	2.5	2.0	1.4	2.7	1.0	1.1	1.4
Hemicelluloses	5.6	17.8	2.3	7.0	10.6	3.6	10.1	0.0	0.0	0.0	0.0	8.9	20.3	2.5	0.0	0.0	3.2
Cellulose	7.9	9.9	11.7	15.6	29.0	19.4	34.7	0.0	0.0	....	0.0	23.4	25.0	0.0	0.0	11.7	0.0
Lignin	5.4	1.6	32.2	21.1	12.5	4.1	27.6	14.1	17.4	....	3.1	20.8	17.3	6.6	8.2	23.6	31.6
Crude protein	50.0	34.9	24.5	16.9	11.1	4.8	4.7	51.7	44.4	89.2	49.9	10.1	6.3	34.4	10.4	16.8	16.2
Ash	3.3	2.5	6.4	9.0	3.4	37.8	1.8	6.6	4.7	2.9	21.6	15.2	8.5	27.7	55.4	34.1	28.5
Moisture	4.9	5.4	5.5	6.3	5.2	4.6	3.8	4.3	5.9	4.6	3.4	3.8	4.0	4.2	5.4	4.1	8.1
Total...	89.2	82.1	93.3	82.4	81.0	80.6	84.6	97.2	88.3	100.9	95.2	90.1	86.7	85.6	89.0	93.8	90.9

analyses of 17 materials therefore, were made by the Waksman method (7). The data are shown in table 4.

As might be expected from its high nitrogen content, dried blood is largely proteinaceous. This material, as well as two of the process tankages (Hynite and Smirow), and acid fish scrap contain no carbohydrate substance but possess varying quantities of resistant carbonaceous substances that are classified under "lignin." The low-protein materials showed, as a rule, correspondingly high proportions of hemicelluloses, cellulose, and lignin. It is the easy decomposability of the first two of these compounds that presumably plays the major role in rendering the nitrogen of these low-protein materials relatively unavailable.

Of the two sludge products analyzed, Milorganite, an activated-sludge product, is high in crude protein, whereas sewage sludge is low in this constitutent, much of its nitrogen having been lost during the anaerobic decomposition process. As would be expected, the availability data show that the activated sludge has a higher nitrogen-fertilizer value than the sludge.

The C–N ratios of washed organics

The C–N ratios of the washed materials are listed in table 2. Carbon was determined by the electric combustion method as described by Fisher (1). In the majority of cases the dividing line between good and poor nitrogen sources was defined by a ratio of about 10. None of the materials whose C–N ratios exceeded this value showed good nitrogen availability by either the vegetative or the nitrification procedure. With the exception of the process tankages, bone meal, beetle molded scrap, and possibly acid fish scrap and animal tankage, those with C–N ratios below 10 showed good nitrogen availability.

To explain the fact that a natural material of a given C–N ratio yields considerably less nitrate than does a synthetic mixture of $(NH_4)_2SO_4$ and cellulose having the same C–N ratio, at least two factors must be considered: the ease of decomposition of the nonprotein carbon compounds present in the nitrogen carrier; and the nitrifiability of the nitrogen in the proteinaceous material itself. The first factor would explain, in part, the low nitrogen availability of materials with ratios greater than 10, and the second would largely explain the wide differences in availability among those of narrow C–N ratio. The insoluble nitrogen compounds in such materials as process tankage and bone meal are apparently very resistant to microbial decomposition, for they not only have a narrow C–N ratio, but contain little carbon of the type whose decomposition could be held responsible for holding up the release of available nitrogen. A third factor, perhaps, should be added: the effect of the possible presence in the organic material of toxic or inhibitory substances.

Of any two materials of narrow C–N ratio containing nitrogen of good availability, the one with the lower C–N ratio normally contains nitrogen of greater availability. Some deviations from this may be explained on the basis of the type of carbon compounds associated with the nitrogen. For instance, the insoluble nitrogen of castor pomace rates virtually the same by the vegetative and the nitrification tests, as does that of cottonseed meal, yet the C–N ratios of these two materials are 9.36 and 5.40, respectively. Castor pomace, however, contains 32.2 per cent lignin to only 5.4 per cent of this constituent for cottonseed meal. Since lignin plays little or no role in depressing nitrification, castor pomace behaves like a material of lower C–N ratio.

In table 5, revised C–N ratios were calculated for various organics, after the lignin carbon was deducted from the total. The carbon content of lignin was assumed to be 57.2 per cent, the same as that of the purified lignin used in formulating the synthetic mixtures of varying C–N ratios. These revised ratios conveniently narrow the gap between castor pomace and cottonseed meal. Castor pomace, Milorganite, and cottonseed meal, the availability of whose nitrogen by the vegetative test lies between 50 and 54 per cent (see table 2), have revised C–N

ratios between 5.05 and 5.76, in place of the original values ranging between 5.40 and 9.36. A revision of these ratios, however, does not always bring the results into line. For example, on the basis of the similarity of their original C–N ratios, the nitrogen of sewage sludge, cocoa meal, Manito humus, and garbage tankage should show smaller differences in availability than the data indicate. The revised ratios do not improve the situation, for the nitrogen of cocoa meal and sewage sludge shows higher availability than does that of Manito humus and garbage tankage, yet the revised ratios of the former materials are wider than those of the latter. It may also be noted that the revised ratios of the process tankages are entirely too narrow for the availability of their nitrogen in comparison with the other organics.

TABLE 5

Nonlignin carbon-nitrogen ratios of washed organic materials

WASHED MATERIAL	NONLIGNIN C–N RATIO	RECOVERY OF ADDED NITROGEN Nitrification test (40 days)	WASHED MATERIAL	NONLIGNIN C–N RATIO	RECOVERY OF ADDED NITROGEN Nitrification test (40 days)
		per cent			*per cent*
Hynite tankage.........	4.06	33	Garbage tankage.......	8.57	0
Smirow.................	5.04	12	Cocoa meal...........	10.6	5
Cottonseed meal........	5.05	57	Sewage sludge.........	11.2	12
Acid fish scrap.........	5.07	50	Alfalfa hay...........	17.5	18
Milorganite.............	5.35	43	Bovung................	17.7	−3
Castor pomace.........	5.76	62	Horse manure.........	25.2	−21
Special soybean meal....	6.90	56	Tobacco stems........	26.2	−9
Manito humus..........	7.05	3	Peanut hull meal.......	35.7	−4

Nitrogen in fractions separated by proximate analysis

Values were obtained for the nitrogen in certain of the fractions separated by the proximate analyses of 17 materials. The data are presented in table 6, where the nitrogen content of each fraction is expressed in percentage of the total nitrogen of the organic ammoniate from which it was derived.

With the exception of acid fish scrap, those washed organics having a crude protein content greater than 20 per cent had more than 50 per cent of their nitrogen extracted by the dilute HCl. None of the materials containing less than 20 per cent crude protein had more than 36.2 per cent of their nitrogen extracted by this treatment. There was a sharp distinction between high- and low-protein materials on the basis of the proportion of nitrogen remaining insoluble after the H_2SO_4 treatment. The high-nitrogen materials had between 2.5 and 8.9 per cent of their nitrogen in this class, whereas the low-nitrogen materials had from 16.1 to 75.5 per cent in the same category. The data for the latter materials tend to indicate that a high resistance of nitrogen compounds to decomposition also plays a part in explaining the poor quality of low-nitrogen sources, since a considerable proportion of the nitrogen of such materials was not

rendered soluble by even the drastic H_2SO_4 treatment during the proximate analysis.

TABLE 6

Separation of nitrogen in washed organic materials

WASHED MATERIAL	TOTAL NITROGEN	FRACTION OF TOTAL NITROGEN					
		Cold water soluble	Hot water soluble	Removed by 2 per cent HCl	Removed by 80 per cent H_2SO_4	Residual nitrogen	Unaccounted for
	per cent	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*	*per cent*
Cottonseed meal	8.70	1.0	7.1	82.2	2.6	2.5	4.6
Special soybean meal	6.43	7.8	5.4	56.8	20.5	4.9	4.6
Castor pomace	5.12	7.5	15.8	54.6	6.5	7.1	8.5
Cocoa meal	2.95	4.2	4.1	25.1	24.5	36.2	5.9
Alfalfa hay	2.19	10.6	8.1	35.2	19.5	16.1	10.5
Tobacco stems	0.88	7.4	5.5	28.5	37.7	29.3	−8.4
Peanut hull meal	0.89	9.1	6.0	36.2	13.6	31.0	4.1
Hynite tankage	10.07	5.0	17.9	59.5	13.6	3.5	0.5
Smirow	7.92	0.9	9.3	70.4	10.2	5.0	4.2
Dried blood	14.66	1.0	1.6	81.6	....	8.6	7.2
Acid fish scrap	8.43	1.5	3.9	34.3	45.2	8.9	6.2
Bovung	1.76	4.5	3.9	22.6	31.7	39.0	−1.7
Horse manure	1.32	10.3	13.0	30.8	14.5	25.0	6.6
Milorganite	6.04	3.5	5.5	51.6	27.2	8.7	3.5
Sewage sludge	1.82	3.6	5.2	18.4	39.2	28.3	5.3
Garbage tankage	2.80	1.7	2.4	6.4	11.7	75.5	2.3
Manito humus	2.71	1.7	2.7	22.7	31.9	41.6	−0.6

TABLE 7

Nitrification of nitrogen derived from water-soluble portions of organic ammoniates

SOURCE OF WATER-SOLUBLE NITROGEN	C–N RATIO	ADDED NITROGEN CONVERTED TO NITRATE		
		20 days	40 days	60 days
		per cent	*per cent*	*per cent*
Urea	0.43	87	88	86
Peruvian guano	0.51	68	84	79
Hoof meal	2.30	57	67	69
Animal tankage	2.53	52	57	58
Special soybean meal	5.07	52	56	64
Tobacco stems	19.8	18	31	33

Nitrification of water-soluble fraction

To study the nitrification of the water-soluble nitrogen of organic ammoniates, five unwashed materials were chosen: animal tankage, special soybean meal, Peruvian guano, hoof meal, and tobacco stems, as all of these contain substantial percentages of water-soluble nitrogen. Cold-water extracts of these organics were prepared, and the nitrogen and carbon contents of these extracts were de-

termined, the carbon being estimated by the wet combustion method (5). Sufficient amounts of the diluted extracts to supply 20 mgm. of nitrogen were then mixed with soil and submitted to the usual nitrification procedure.

The carbon-nitrogen ratios of the soluble fractions, including urea, and the nitrification data for their nitrogen are given in table 7. The nitrification of the soluble nitrogen from tobacco stems and animal tankage was considerably greater than that from their water-insoluble counterparts (table 2). With the special soybean meal, hoof meal, and Peruvian guano there appeared to be little difference between the nitrification of the water-soluble and of the water-insoluble nitrogen, any slight differences that existed being in favor of the former. With

TABLE 8

Nitrification of nitrogen of unwashed organic ammoniates as calculated from data on water-soluble and water-insoluble portions

SOURCE OF NITROGEN	ADDED NITROGEN CONVERTED TO NITRATE		
	20 days	40 days	60 days
	per cent	*per cent*	*per cent*
Special soybean meal			
Found..	61	66	..
Calculated...................................	51	56	60
Tobacco stems			
Found...	−14	5	6
Calculated...................................	1	10	15
Hoof meal			
Found..	65	68	..
Calculated...................................	57	62	65
Animal tankage			
Found..	37	45	..
Calculated...................................	35	45	48
Peruvian guano			
Found..	80	77	..
Calculated...................................	67	79	79

the water-soluble nitrogen, a close relation existed between the C–N ratio and the nitrification value.

The nitrification of the nitrogen of both the water-soluble and the water-insoluble portions of five organics being known, a calculation was made of the nitrification to be expected from the unwashed organics, the relative proportions of water-soluble and water-insoluble nitrogen in the unwashed material being used. The comparison between the values found and those calculated is made in table 8. There is fair agreement, especially with the nitrification of the nitrogen of animal tankage at 20- and 40-day periods, and with that of Peruvian guano at the end of 40 days.

CONCLUSIONS

The results obtained indicate that the principle of the C–N ratio may be applied with success in interpreting the availability behavior of many organic am-

moniates. This seems to be especially true of water-soluble nitrogen. In the water-insoluble fractions, ease of decomposition and relative abundance of the associated carbonaceous material must be considered, as well as the decomposability of the insoluble nitrogenous material itself, before a rigid application of C–N ratios to availability can be made. The insoluble nitrogen of process tankages and bone meal is of poor availability not because of unfavorable C–N ratios but because of resistance to decomposition of their nitrogen-containing compounds. The similar behavior of washed low-nitrogen materials may be due partly to the same property and partly to the presence of large amounts of easily decomposable carbon.

SUMMARY

A series of 34 organic ammoniates and waste organic materials were tested with regard to the availability of their nitrogen. Ratings, particularly of their insoluble nitrogen, were made of these materials by vegetative, nitrification, and permanganate methods. A study was then made as to the applicability of the principle of the C–N ratio in explaining the estimated availability of the nitrogen of these materials. This principle proved to be a valuable supplemental aid in determining the quality of the nitrogen in these materials. In some cases, it was found necessary to apply a correction to the C–N ratio by eliminating the carbon of the lignin in the material. For certain materials, however, the application of this correction factor failed to bring the products into line with the known availability of their nitrogen.

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THE DISTRIBUTION OF MINERAL ELEMENTS IN THE SUGAR BEET AS INFLUENCED BY DIFFERENT PRECEDING CROPS[1]

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The only quantitative method for following the movement of mineral nutrients into plants consists in measuring the actual weights of the various elements at progressive stages of plant growth. This is accomplished by determining the percentage composition of the plant tissues as well as the average dry weight per plant at each date of sampling. In the present study, such procedure was followed to evaluate differences in the assimilation of minerals by sugar beets after different preceding crops.

Few investigators have worked with mineral assimilation rates of sugar beets. Irving, of Canada (5), reported some work but did not include all the important cations. Cerny (2) studied the composition of sugar beet tops and roots at successive dates but did not report his work in terms of mineral assimilation rates or levels.

METHODS AND MATERIALS

The plot of ground selected for this investigation consisted of two $\frac{1}{4}$-acre plots at the Huntley Field Station, Huntley, Montana, on irrigated land. The soil has an average texture of 33 per cent sand, 40 per cent silt, and 27 per cent clay, and contains about 0.18 per cent carbonate carbon, 0.59 per cent calcium, 0.55 per cent potassium, 0.51 per cent magnesium, 0.06 per cent sodium, and is very low in organic matter and nitrogen.

It was cropped to alfalfa for 3 years, after which four $\frac{1}{8}$-acre plots were laid out. Single plots were planted to potatoes, beans, alfalfa, and sugar beets, for four seasons. When these crops were harvested, no crop residues were left on the soil of the sugar beet and bean plots, only stubble was left on the alfalfa plot, and all crop residues were left on the potato plot. Estimated phosphoric acid and nitrogen removals for the 4-year period are presented in table 1. Succeeding this 4-year period, the whole field was fall-plowed, prepared, and planted to sugar beets on May 11 of the following year. The study was made on this crop of sugar beets. The calculated acre yields of clean beets were as follows: 17.5 tons on the potato plot; 15 tons on the bean plot; 9.5 tons on the alfalfa plot; and 8.5 tons on the beet plot.

The average soil and air temperatures for periods between samplings are summarized in table 2.

Sampling

Samples were collected—on June 16, July 11, August 7, September 3, and October 16—only from areas where plant competition was normal, and consisted of an average of 90 plants on each date. The sugar beets collected were immediately cleaned, topped, and weighed separately as tops and roots. Representative samples of these materials were then weighed, dried in a force-draft oven at 60°C. for several days, and reweighed. This final weight and the true dry matter determination were used to calculate the total dry matter obtained in each case. The dried sample was ground and otherwise prepared for mineral analyses and other determinations.

TABLE 1
Removals of N and P_2O_5 from soil by crops preceding sugar beets

CROP FOR 4-YEAR PERIOD	N REMOVAL BY CROP	P_2O_5 REMOVAL BY CROP
	lbs.	*lbs.*
I. Potatoes	125	45
II. Beans	...	180
III. Alfalfa	...	145
IV. Sugar beets	200	40

TABLE 2
*Average soil and air maximum and minimum temperatures between sampling dates**

PERIOD	SOIL		AIR	
	Max.	Min.	Max.	Min.
	°F.	°F.	°F.	°F.
May 11–June 17	68	50	73	44
June 17–July 7	73	63	85	54
July 7–August 8	82	63	88	54
August 8–September 4	63	55	80	42
September 4–October 17	43	37	62	37

* Records kept by the Huntley Field Station and the botany and bacteriology department of Bozeman at the site of the plots.

Analysis

Dry matter. Moisture determinations were made on the air-dried material by heating weighed samples at 98°C. for 5 hours in a vacuum oven. All mineral concentrations are calculated on this dry matter basis.

Nitrogen. Total nitrogen was determined by the Kjeldahl method using metallic Hg as a catalyst.

Phosphorus was determined colorimetrically after washing in $HClO_4$ and HNO_3 (8).

Sulfur was determined by neutralizing an aliquot of $HClO_4$-HNO_3 digest with ammonia, making slightly acid with HCl, and precipitating with $BaCl_2$.

Potassium was determined from an aliquot by the sodium cobaltinitrite method,[2] all $HClO_4$ and ammonia being removed before analysis.

Sodium was determined from an aliquot by the uranyl zinc acetate method (7).

Calcium was determined from an aliquot by the official method (1).

Magnesium was determined by the official method (1).

Acid-insoluble ash was determined by igniting and weighing the insoluble residue remaining after $HClO_4$-HNO_3 treatment.

Total ash was determined by the loss in weight due to ignition at 600°C. for 1 hour.

<div align="center">RESULTS</div>

A single plant is the basis for calculation of minerals assimilated on each sampling date. These data, presented in table 3, represent the multiple of parts per 100 of constituent and milligrams of dry weight. The percentage composition of each mineral, reported in table 4, is based on true dry matter. The ratios of each element in tops (including crowns) to roots are shown in table 5, in such units that the sum of these two quantities equals 100. The relative intensity of each cation against the other three, reported in table 6, is also in such terms that the sum of these quantities equals 100.

<div align="center">*Dry matter*</div>

The average dry weight of individual plants increased to the last date of sampling (table 3). With few exceptions, the percentage of dry matter in fresh plants (table 4) also showed gradual increase in successive samples; the greatest change occurred after the September 3 sampling. On August 7, tops accounted for an average of 72.5 per cent of the total growth and varied from 68 per cent on plots with preceding crops of potatoes and beans to 77 per cent on plots with preceding crops of alfalfa and sugar beets (table 5). On the final sampling date top growth accounted for an average of only 41.2 per cent of the total growth and varied from 36 per cent for plots with a preceding crop of potatoes to 47 per cent for plots with a preceding crop of alfalfa. An average of 75 per cent of the total leaf growth had occurred by September 3 after beans and potatoes, but an average of only 55 per cent had occurred on the same date after beets and alfalfa. A considerable portion of the total root growth occurred after the September 3 sampling on all plots. Although the most effective top to root ratio existed on October 16 on the plot on which potatoes preceded, this amounted to 20 per cent more tops than was required to produce the same size beet, grown simultaneously and with properly balanced phosphorus and nitrogen fertilization.

<div align="center">*Constituents principally absorbed as anions*</div>

Nitrogen. In this experiment the whole plant usually showed an increase in nitrogen between successive dates of sampling (table 3). On plots with preceding crops of beans and potatoes, which produce conditions for early nitrogen

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[2] Willcox. 1933 Methods of Analysis used in the Rubidoux Laboratory, Riverside, California. (Mimeo.)

TABLE 3

Average chemical composition of entire sugar beet plant on each sampling date

In milligrams of dry matter per plant

PRECEDING CROP*	JUNE 16	JULY 11	AUGUST 7	SEPTEMBER 3	OCTOBER 16
			Total dry matter		
I	162	24,510	77,500	131,800	191,400
II	82	13,480	55,400	83,700	181,900
III	54	2,960	42,470	82,600	138,300
IV	57	5,290	7,570	34,600	121,700
			Nitrogen		
I	7.4	666	2,150	2,270	2,200
II	3.2	401	1,770	1,740	1,910
III	2.5	135	1,290	1,440	2,020
IV	2.3	225	247	629	1,668
			Phosphorus		
I	0.41	63	147	183	202
II	0.14	29	131	116	188
III	0.14	10	76	69	128
IV	0.14	16	13	31	120
			Sulfur		
I	0.63	62	179	232	374
II	0.38	48	177	198	284
III	0.22	9	109	258	310
IV	0.26	13	27	100	338
			Acid-insoluble ash		
I	1.23	522	974	2,020	3,660
II	0.43	303	729	1,820	2,885
III	0.16	48	699	975	2,310
IV	0.31	86	148	947	2,790
			Potassium		
I	8.1	646	1,230	1,760	2,570
II	4.2	402	1,120	1,010	2,670
III	2.3	950	1,050	1,465	2,160
IV	2.4	134	179	743	1,850
			Sodium		
I	4.2	537	2,080	3,040	2,090
II	2.0	327	1,420	1,657	2,145
III	1.2	52	1,080	1,850	2,230
IV	1.4	93	222	642	1,605
			Calcium		
I	2.7	166	334	440	902
II	1.8	129	274	573	634
III	0.97	203	284	1,040	845
IV	0.88	30	70	309	642
			Magnesium		
I	1.8	159	333	429	596
II	1.0	98	235	402	524
III	0.63	18	228	682	634
IV	0.55	29	50	177	465

* I — Potatoes   III — Alfalfa

PRECEDING CROP†	JUNE 16	JULY 11		AUGUST 7		SEPTEMBER 3		OCTOBER 16	
	Total plant	Tops	Roots	Tops	Roots	Tops	Roots	Tops	Roots
Dry matter									
I	9.0	8.7	12.6	9.3	10.5	10.1	14.6	15.5	20.6
II	8.9	9.3	12.4	8.7	13.1	8.9	15.8	14.5	21.2
III	12.6	12.1	15.4	13.1	12.0	9.4	15.6	13.4	21.1
IV	12.7	10.4	9.8	8.0	11.7	10.5	21.6	14.5	23.3
Nitrogen									
I	4.6	3.6	1.2	3.4	1.4	2.6	1.0	2.0	0.67
II	3.9	3.6	1.2	4.1	1.3	3.0	0.92	1.7	0.62
III	4.7	5.4	1.2	3.6	1.1	2.4	0.80	2.2	0.81
IV	4.1	5.5	1.1	3.9	1.1	2.7	0.84	2.2	0.74
Phosphorus									
I	0.251	0.316	0.160	0.229	0.105	0.186	0.087	0.167	0.071
II	0.176	0.248	0.123	0.300	0.104	0.189	0.077	0.151	0.073
III	0.261	0.372	0.146	0.206	0.080	0.102	0.056	0.136	0.054
IV	0.243	0.383	0.119	0.187	0.091	0.122	0.055	0.141	0.067
Sulfur									
I	0.39	0.32	0.14	0.28	0.12	0.30	.076	0.43	0.062
II	0.46	0.44	0.12	0.42	0.11	0.36	.083	0.32	0.051
III	0.42	0.36	0.12	0.30	0.10	0.47	.084	0.40	0.069
IV	0.46	0.30	0.12	0.43	0.088	0.47	.090	0.55	0.071
Acid-insoluble ash (SiO_2)									
I	0.76	2.3	1.8	1.7	0.35	2.7	0.58	2.7	1.5
II	0.53	2.8	0.72	1.6	0.71	3.3	0.78	2.8	0.78
III	0.30	1.7	1.4	1.9	0.76	1.7	0.43	3.0	0.50
IV	0.54	1.7	1.4	1.6	3.2	3.4	2.0	4.0	1.0
Potassium									
I	5.0	3.1	1.8	1.8	1.2	2.2	0.63	2.5	0.69
II	5.1	3.5	1.5	2.5	1.0	1.5	0.64	2.6	0.78
III	4.2	3.5	2.1	2.8	1.4	2.5	0.73	2.6	0.65
IV	4.3	2.8	1.9	2.7	1.2	3.1	1.1	2.7	0.63
Sodium									
I	2.6	3.0	0.72	3.3	0.97	3.2	1.6	2.2	0.44
II	2.4	3.0	0.69	3.3	1.0	2.9	0.78	2.3	0.44
III	2.2	2.0	0.62	3.0	0.96	3.2	0.82	2.8	0.54
IV	2.5	2.2	0.57	3.5	0.97	2.9	0.65	2.4	0.46
Calcium									
I	1.7	0.97	0.17	0.58	0.10	0.61	0.10	1.2	0.063
II	2.1	1.2	0.18	0.66	0.15	1.1	0.17	0.8	0.054
III	1.8	0.81	0.21	0.81	0.18	2.0	0.13	1.2	0.083
IV	1.6	0.72	0.18	1.1	0.22	1.5	0.21	1.1	0.084

TABLE 4—*Concluded*

PRECEDING CROP†	JUNE 16	JULY 11		AUGUST 7		SEPTEMBER 3		OCTOBER 16	
	Total plant	Tops	Roots	Tops	Roots	Tops	Roots	Tops	Roots
Magnesium									
I	1.1	0.85	0.30	0.50	0.18	0.43	0.26	0.51	0.20
II	1.2	0.90	0.25	0.54	0.19	0.68	0.24	0.50	0.16
III	1.2	0.69	0.37	0.63	0.22	1.3	0.15	0.69	0.25
IV	0.97	0.64	0.31	0.75	0.33	0.79	0.20	0.64	0.18
Total ash									
I	26.6	25.2	8.2	24.7	6.7	20.4	6.2	19.3	4.0
II	25.9	24.1	7.0	22.3	7.1	23.1	5.4	16.7	4.0
III	27.8	19.0	9.2	22.0	6.6	25.9	5.2	23.0	6.0
IV	23.7	17.0	7.5	22.7	7.3	22.3	7.8	20.3	4.8

absorption, the sugar beet plants assimilated, by the August 7 sampling, average of 94 per cent of all the nitrogen absorbed. On the plot with a preceding crop of alfalfa, only 64 per cent, and on the plot growing sugar beets continuously, 14.8 per cent, had been absorbed by this date. This variation may have been due to delayed availability of nitrogen after the alfalfa and beet crops on this soil. When the size of beet roots and the maximum amount of nitrogen absorbed up to the last sampling date on these plots are compared to corresponding beet root sizes and nitrogen absorptions on simultaneous fertilizer experiments, an excess of this element occurred in the whole plant after each preceding crop. This excess amounts to an average of 28 per cent on the plots with preceding potatoes and beans, and an average of 78 per cent on the plots with preceding beets and alfalfa.

Though an actual intake of nitrogen was realized between dates of sampling, a decrease in nitrogen concentration was equally apparent. This decrease was most abrupt after beans and potatoes.

Nitrogen as a whole was associated with top growth, though as high as 37 per cent of the total nitrogen occurred in the roots of the largest beets. Up to the September 3 sampling, a very small proportion of the total nitrogen occurred in the roots on plots with preceding crops of alfalfa and beets. This is due only in part to the relatively small roots, since the concentration is also below that of the other two plots.

Phosphorus. The amounts of phosphorus absorbed varied more between plots than did nitrogen, and on the last day of sampling this variation correlated grossly with the yield of root. By August 7, the plants from plots that had previously grown beans and potatoes had already assimilated an average of 61.5 per cent of the total phosphorus absorbed during the experiment, whereas the plants on plots that had grown alfalfa and beets had assimilated only 59 and 11 per cent. On the basis of a fertilizer experiment run simultaneously and with the same sampling technique, the amounts of phosphorus absorbed by the last

TABLE 5

Distribution of minerals between tops and roots of sugar beets on each sampling date

PRECEDING CROP*	JULY 11		AUGUST 7		SEPTEMBER 3		OCTOBER 16	
	Tops	Roots	Tops	Roots	Tops	Roots	Tops	Roots
Dry matter								
I	63	37	68	32	45	55	36	64
II	74	26	68	32	55	45	39	61
III	80	20	77	23	59	41	47	53
IV	72	28	77	23	53	47	43	57
Nitrogen								
I	84	16	84	16	68	32	63	37
II	89	11	87	13	80	20	64	36
III	94	6	92	8	81	19	71	29
IV	93	7	93	7	78	22	69	31
Phosphorus								
I	77	23	83	17	60	40	58	42
II	85	15	85	15	76	24	57	43
III	92	8	90	10	73	27	69	31
IV	88	12	87	13	71	29	62	38
Sulfur								
I	80	20	83	17	89	11	80	20
II	91	9	89	11	85	15	80	20
III	92	8	91	9	89	11	84	16
IV	86	14	94	6	86	14	86	14
Acid-insoluble ash (SiO_2)								
I	68	32	91	9	79	21	51	49
II	92	8	83	17	84	16	71	29
III	84	16	90	10	85	15	73	27
IV	75	25	63	37	65	35	75	25
Potassium								
I	74	26	77	23	74	26	68	32
II	86	14	83	17	76	24	69	31
III	88	12	88	12	83	17	78	22
IV	79	21	88	12	77	23	77	23
Sodium								
I	88	12	84	16	63	37	74	26
II	93	7	87	13	83	17	77	23
III	92	8	92	8	85	15	83	17
IV	91	9	93	7	83	17	80	20
Calcium								
I	91	9	92	8	82	18	92	8
II	94	6	90	10	89	11	91	9
III	94	6	94	6	96	4	93	7
IV	91	9	95	5	89	11	91	9
Magnesium								
I	83	17	79	21	59	41	59	41
II	91	9	86	14	78	22	67	33
III	90	10	91	9	93	7	71	29
IV	83	17	88	12	81	19	73	27

*I = Potatoes   III = Alfalfa

sampling date on plots with these preceding crops produced slightly more weight of beet roots. This is some proof that the first limiting growth factor was phosphorus on all plots.

Like nitrogen, phosphorus generally tends to decrease in concentration with successive samplings, and this change is most pronounced after beets and alfalfa.

TABLE 6

Ratio of cations in tops and roots of sugar beets on each sampling date

Based on percentage composition

PRECEDING CROP*	JUNE 16	JULY 11		AUGUST 7		SEPTEMBER 3		OCTOBER 16	
	Total Plant	Tops	Roots	Tops	Roots	Tops	Roots	Tops	Roots
Potassium									
I	49	39	60	29	50	34	25	38	49
II	47	41	58	36	43	26	35	40	54
III	45	49	64	38	50	28	40	35	43
IV	46	44	65	33	44	27	50	40	46
Sodium									
I	25	38	24	54	39	50	61	35	32
II	22	35	26	47	43	46	53	38	31
III	24	29	19	42	35	36	45	40	36
IV	27	35	19	44	36	36	31	35	34
Calcium									
I	16	12	6	9	4	9	4	19	5
II	20	14	7	9	6	17	9	16	5
III	19	12	6	11	7	22	7	16	5
IV	17	11	6	14	8	18	10	16	6
Magnesium									
I	10	11	10	8	7	7	10	8	14
II	11	10	9	8	8	11	13	9	11
III	12	10	11	9	8	14	8	9	16
IV	10	10	10	9	12	9	9	9	14

*I = Potatoes   III = Alfalfa
II = Beans   IV = Sugar beets

Leaf symptoms of phosphorus deficiency occurred only after these two crops and in highest incidence at the August 7 sampling.

Although most of the phosphorus remains in the tops up to the last date of sampling, a higher percentage is found in the roots than is the case with nitrogen.

Sulfur. Accumulation of sulfur in the whole plant occurred principally after the August 7 sampling. This amounted to 38, 52, 65, and 87 per cent of the total sulfur absorbed from plots that had grown beans, potatoes, alfalfa, and sugar beets respectively. A lesser portion of the total phosphorus and nitrogen were absorbed after August 7.

Very similar percentages of sulfur and phosphorus occurred in the roots on all dates of sampling, thus the variation in assimilation was exclusively due to the tops, where considerably more sulfur than phosphorus is present in all samples after July 11. The average sulfur to phosphorus ratio in the October 16 samples of tops was 2.88, whereas this ratio was but 0.86 on July 11. The ratio was higher in those beets showing leaf symptoms of phosphorus deficiency.

Sulfur occurred principally in the tops, and the ratio of top content to root content in samples taken on September 3 and October 16 was higher than was the case for either nitrogen or phosphorus.

Acid-insoluble ash. Although the acid-insoluble ash comprises a considerable portion of the total minerals taken in, it probably is functionless. There is likewise no definite pattern or trend in the concentration of this constituent in the dried plant tissue. The quantity increases between dates of sampling, and an average of 78 per cent of the total amount absorbed was taken in after the August 7 sampling. Its distribution in roots and tops does not follow any perceptible pattern except that it is found principally in the tops.

Constituents absorbed as cations

Potassium. Potassium increases in the whole plant on successive sampling dates. In fact, it is absorbed principally after the August 7 sampling. The amount absorbed after this date ranges from 52 per cent on plots on which potatoes preceded beets to 90 per cent on plots with continuous beets.

Unlike phosphorus and nitrogen, potassium tended to maintain a constant concentration in the dry matter after the August 7 sampling. It tends to be more concentrated in top samples from beet or alfalfa plots than from bean or potato plots. This trend also occurs, though to a lesser extent, in the root samples.

The average ratio of potassium to the other three cations in top samples and in root samples was at a minimum on September 3. This same intensity trend occurred in leaf samples taken on other plots during the 1939 and 1940 growing season. A general inverse relation appeared between the potassium intensity with relation to the other cations in the tops and the rate of top growth.

Sodium. Sodium was absorbed in appreciable quantities throughout the growing season and even exceeded potassium on some dates of sampling. There was a striking constancy in the ratio of nitrogen to sodium in the whole plant on *each date of sampling*. On June 16, there was an average of 1.78 times as much nitrogen as sodium, with limits of 1.60 to 2.08; on July 11, 1.14 times as much nitrogen as sodium occurred, with limits of 1.04 to 1.19; and on October 16, 0.98 times as much nitrogen as sodium occurred, with limits of 0.89 to 1.05. Although this ratio tended to decrease with development of the plant, an association between these two elements in this type of soil seems to exist.

Unlike potassium, sodium tended to increase in the dry matter up to mid-season and dropped off by the end of the season to a level almost identical to that found in samples taken June 16. It was found in higher concentration in some cases following beans and potatoes, as compared with alfalfa and beets, but this was not constant for the whole season.

Sodium tended to concentrate in the tops to a greater extent than potassium. Though a function for sodium has probably not been established with sugar beets, Lehr (6) claimed that it has a definite place in the leaf physiology of this plant, and that this role was not simply a substitution for some of the functions of potassium. Sodium seemed to distribute itself between tops and roots in a manner very similar to that of nitrogen.

The ratio of sodium to the other cations gave it prominence at the August 7 and September 3 sampling dates, when potassium is less prominent. This inverse relation may strengthen a theory that partial replacement of potassium by sodium is possible. It is probably at midseason that soluble sodium salts present in measurable quantities could be more easily assimilated than could potassium. In this respect it is interesting to note that the highest ratio of sodium to the other ions occurs on land that had grown potatoes, and this proved the most productive. Conversely, the plot on which beets had grown continuously showed the lowest ratios and the poorest productivity. A general positive correlation existed between the intensity of sodium among the other cations found in the tops and the rate of top growth.

Calcium. Calcium was absorbed throughout the season, but an average of 69 per cent was absorbed after the August 7 sampling. A greater percentage than of any of the other cations studied, was absorbed after this date.

The percentage concentration of calcium in the tops as compared with that in the roots was high at the beginning and at the end of the season and declined sharply at the August 7 sampling. The least variation occurred on the plot with continuous beet growth; the most, with preceding beans. Root samples of all four plots showed a steady decline in concentration from the first samples. Crops on plots with continuous beets and with preceding alfalfa showed a higher concentration than the crops on the other plots at the end of the season.

Calcium was concentrated in the tops to a greater extent than any of the other cations studied. If the principal function of calcium is to neutralize acids formed by physiological metabolism, then certainly the leaf is almost exclusively the area of acid concentration.

The ratio of intensity of calcium to the other three cations in the leaves was at a minimum on the August 7 sampling and increased to a maximum by September 3 on all plots except those with preceding potatoes. The change in concentration is inverse to that of potassium in every case between August 7 and September 3.

Magnesium. Magnesium is absorbed rather uniformly throughout the season, though more of it is absorbed after August 7 than before. This amounts to an average of 64 per cent of the total magnesium absorbed but varies from 45 per cent for the plot with preceding potatoes to 90 per cent for the plot with continuous beets. The rates of absorption of potassium and magnesium on successive dates correlated somewhat, but only about one-fourth as much magnesium as potassium is present. The decline in magnesium concentration in the tops continues to the end of the season. No rise similar to that of calcium occurs.

Less magnesium than calcium is found in the tops, but a higher percentage of magnesium is present in the root tissue. The average magnesium to calcium

ratio of root tissue is 1.66 on July 11, 1.40 on August 7 and September 3, and 2.78 on October 16. The sharp increase on the last date of sampling is due not to an alteration of the concentration of magnesium but rather to a sharp decline in calcium concentration.

A much higher proportion of the magnesium in sugar beet plants occurs in the roots than in the case of calcium.

Potassium and magnesium appear to be distributed similarly between tops and roots. This seems significant, since the rates of absorption also have been shown to correlate. Magnesium tends to be present to a greater extent in the roots after potatoes than after any of the other crops, particularly alfalfa.

There is less variation in the ratio of magnesium or calcium to the other cations than in that of sodium or potassium. The concentration of magnesium in the soil is approximately the same as that of calcium and potassium.

DISCUSSION

It is probable that the difference in growth of sugar beets after the four crops, potatoes, beans, alfalfa, and beets, is due to alterations of nutrient availability by direct or indirect means. This is no new concept, since it is one of the principles of crop rotation. It was pointed out by Hartwell and co-workers (3, 4) in an extensive, well-controlled experiment. It is unfortunate, however, that they did not discover what nutrient alterations had occurred to bring about such a variance in productivity.

The difference in amount of root dry matter produced on the four plots in the present study was not directly related to the removals of phosphorus by the preceding crops. For example, four years of continuous beans removed about 180 pounds of P_2O_5, and sugar beets during the same period removed but 40 pounds, yet root dry matter and phosphorus content of sugar beets after beans were significantly higher than on the continuous beet plot. The superiority of one preceding crop over another, then, is quite independent of the removals of minerals, at least for a short-time experiment.

The growing season included in this investigation was shorter than is considered desirable. The season after September 1 was of little value in the growth of sugar beets. Undoubtedly, if the experiment were repeated with a longer season some changes in the nutrition of the crop could be anticipated.

Sugar beets grown for this investigation were, with few exceptions, still assimilating most of the plant nutrients at the time of the last sampling. In order of decreasing absorption rates between the last two sampling dates were silica, potassium, sulfur, phosphorus, magnesium, calcium, nitrogen, and sodium. Other studies on sugar beets using the same sampling methods have shown some of these nutrients as ceasing to be absorbed or as being lost from the plant by this last sampling date. These elements included sodium, nitrogen, magnesium, and potassium. It is probable that the continued absorption of elements on these four plots was due to excess available nitrogen in the soil or to relative immaturity of the crop toward the end of the season, especially on preceding alfalfa and continuous beet land.

It is probable that phosphorus limited the extent of growth, particularly of

roots, after each of the preceding crops. The soil in which this experiment was run, with few exceptions, responds by increased growth of sugar beets when this element is added. The full explanation of this fact is obscure, though undoubtedly the type of crop preceding sugar beets changes the amount of phosphorus available. In this experiment, about 1.7 times as much phosphorus was absorbed by sugar beets following potatoes as when beets were grown continuously. There is also a great variation in the time when this element was absorbed on these two plots. The bulk of all the phosphorus absorbed on continuous beet land (74 per cent) was taken up after September 3, whereas but 9 per cent was removed after this date from land previously in potatoes. Similar, though less marked, variations occurred on the other plots. Nitrogen also varied in the time of principal absorption, but this element correlated with phosphorus. This would indicate either that microflora and the decay of residues during the season present a rather constant ratio of nitrogen and phosphorus in available form, or that the plant is capable of maintaining some semblance of balance in the absorption of these two elements.

The significant absorption of sulfur on all of the plots late in the season and the concentration of this nutrient principally in the leaves and crowns may indicate that a substitution of this element for phosphorus was attempted in the leaf tissue. It is probable that absorption of sulfur on this soil is in luxury amounts, since the area has some soluble sulfates present in the soil solution throughout the growing season. When compared to potatoes all of the other preceding crops caused greater concentration of all of these elements in the sugar beet tops. This may have been caused by the excess of nitrogen, which increased the growth of tops, and since the phosphorus content of the roots was low, less of these other elements could be present.

The most obvious variations in the average ratio of cation concentrations on the same date of sampling occurred with sodium and potassium. The ratios given for these two elements are similar only on the July 11 and October 16 samplings. Between these dates the sodium ratio is much higher than that of potassium. On the basis of top composition these variations are principally due on the one hand, to the decline in potassium concentration to a rather constant level by August 7, and, on the other hand, to a rise in sodium to a maximum concentration by August 7, followed by a decline to a level similar to that of seedling beets by October 16. It is probable that these variations in sodium and potassium are normal for plants grown on this type of soil. This same trend has occurred in leaf samples taken throughout other growing seasons and on widely scattered plots. Root tissue showed a considerable deviation from the average ratio of composition for these two elements on September 3, but otherwise very similar percentages occurred in sugar beets from these four plots. Though calcium and magnesium do not appear to vary greatly, according to data compiled in table 6, composition percentages present a different picture. This is principally due to the relatively low intensity of these two ions compared with sodium and potassium.

The extent to which magnesium is associated with the root during the latter

part of the season is noteworthy in comparison with the low amount of calcium found there at this stage of growth. It is possible that magnesium here acts to keep phosphorus mobile either in translocation to the top or in return to the root.

In general, it seems plausible that the application of nutrients to supplement probable deficiencies should require a careful study of this kind. Such a study would determine the relative absorbing power and requirements of the species, as well as the time when application of deficient elements could best meet the needs of the plant. If, for example, the phosphorus requirement to produce a definite sized beet could be determined, along with the available supply of the soil and the availability of the nutrient when added, one would certainly have a rational system for nutrient applications.

SUMMARY

The nutrition of sugar beets as influenced by four different preceding crops was followed progressively through the growing season.

Calculated acre yields of clean beets were 17.5 tons on potato ground, 15 tons on bean ground, 9.5 tons on alfalfa ground, and 8.5 tons on beet ground.

With few exceptions, the amounts of all minerals increased from the first to the last sampling.

The early rapid absorption of nutrients by sugar beets after beans and potatoes seems noteworthy; perhaps this factor accounts for the superiority of these two as preceding crops.

The limiting factor of growth after the four preceding crops appeared to be phosphorus; the severity was greatest after alfalfa and beets, and least after beans and potatoes.

It is possible that the delayed absorption of minerals after alfalfa could be eliminated by allowing the stubble more time to decompose before planting sugar beets.

The cation balance in tops and roots is altered by growth of different preceding crops. This may be due to the change in physiological conditions instituted in this soil by the crop or by changes in anion availability.

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DEPHOSPHORYLATION OF ORGANIC PHOSPHORUS COMPOUNDS BY SOIL CATALYSTS[1]

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Previous experiments (13, 14) revealed that plant roots possess exoenzyme systems, which originate in the cellular material normally released to the rhizosphere during plant growth. It appeared that the release of these root-borne catalysts to the soil would have a direct bearing on fertility problems and, in view of this fact, soil was examined to determine whether it possessed catalytic properties similar to roots. This investigation was made to determine whether soils show phosphatase activity independent of an active micropopulation, and if so, to compare the properties of such catalysts with the characteristics of the root-borne enzymes.

The discovery of a vigorous phosphatase activity of corn and tomato roots (14) and the reports of Conrad (2, 3) of thermolabile soil catalysts capable of decomposing urea independently of microbial activity, suggest that soils may contain a variety of catalysts, one source of which may be the residues of both actively growing and dead plant roots. No report was found of phosphatase activity in sterile soils similar to that shown for urease by Conrad (2), but some of the studies on rates of decomposition and penetration of organic phosphates offer indirect evidence of the effects of such catalysts (5, 7, 10, 11, 15, 16).[3] Some of these related investigations will be discussed in connection with the results of this study in a later section.

EXPERIMENTAL MATERIALS AND METHODS

A planosol, Ames fine sandy loam (8), was used in these studies principally because it was low in organic and total phosphorus. The area from which the samples were taken in the fall of 1941 had been in corn the previous summer and also during 1940. The untreated soil contained 91 and 190 p.p.m. of organic and total phosphorus, respectively, and had a pH of 5.6.

All acidity measurements were made with a Coleman glass electrode pH meter, 1:2 soil-water suspensions being employed for the soil tests. Buffer curves were

run on the soil–organic-phosphate suspensions prior to dephosphorylation tests, dilute H_2SO_4 and NH_4OH being used to adjust the suspensions to the desired reactions. The method of preparation and the source of the stock solutions of calcium glycerophosphate and nucleic acid were as previously described (13). Only freshly prepared solutions of nucleic acid were used.

Effectiveness of toluene as a soil sterilizing agent

Preliminaty tests were made to determine the effectiveness and suitability of toluene for inhibiting the activity of soil microorganisms under the conditions of these studies. Varying amounts of toluene were added to samples of the soil with and without calcium glycerophosphate. Sucrose was added to some samples before incubation and to some after 24 hours' incubation. The evolution of carbon dioxide at 24-hour intervals was measured by the method described

TABLE 1

Carbon dioxide evolution from toluene-treated soil

TREAT-MENT NUMBER	TREATMENT	CO_2 EVOLVED		
		0–24 hrs.	24–48 hrs.	48–72 hrs.
		mgm.	*mgm.*	*mgm.*
1	100 gm. soil plus calcium glycerophosphate (100 p.p.m.P)	28.0	17.0	12.0
2	Same as treatment 1, plus 1 per cent sucrose*	85.1	84.0	105.5
3	Same as treatment 1, plus 9 cc. toluene	1.2	3.4	2.4†
4	100 gm. soil plus 9 cc. toluene	2.5	2.5‡	2.5†

* One gram of sucrose if completely oxidized is equivalent to 1500 mgm. of CO_2
† Added sucrose after second 24 hours.
‡ Added calcium glycerophosphate after 24 hours.

by Norman and Newman (9). The results in table 1 show the effectiveness of toluene as an antiseptic. Since no increase in CO_2 evolution resulted from adding sucrose to the toluene-treated soil after 24 hours' incubation either with or without calcium glycerophosphate, it is believed that the toluene treatment was sufficiently effective to warrant its use as a sterilizing agent in these studies. A small amount of toluene (3 cc./100 gm. soil) was as effective as higher concentrations.

Toluene has been widely used by investigators to inhibit microbial activity with a minimum effect on enzyme action. Quastel and Wooldridge (12) reported that a heavily inoculated culture of *Escherichia coli* was completely sterilized by treatment with 15 per cent toluene for 5 minutes at room temperature.

Technique for studying the activity of soil catalysts

Two-gram portions of screened air-dry soil were placed in small glass sample bottles and 0.3 cc. of toluene was added. The bottles were stoppered and the contents mixed and left standing 30 minutes before adjustment of the pH and

addition of the toluene-saturated organic phosphate solutions. Finally, the volume of the suspensions were adjusted with distilled water to give a 1:2 soil-liquid suspension, the bottles were restoppered, the contents were mixed, and incubation was started immediately. Controls with soil-water suspensions adjusted to similar pH values, and organic phosphorus solutions alone, were run.

In tests in which all the incubations were carried out at one temperature a shaker was used to agitate the samples continuously during incubation. Agitation of samples in the oven was accomplished by mounting a small stirring motor on top of the oven and connecting it through an air vent to a tilting platform inside, to which the bottles of soil suspensions were fastened.

Phosphorus mineralization was measured by increases in inorganic phosphorus in filtrates, which were obtained by extracting the soil after incubation with three 1-cc. portions of 10 per cent HCl and washing with water. Though it is recognized that some fixation of the inorganic phosphorus released from the organic compounds may have taken place, it is believed that the amount which would resist extraction by the method used would be small. Additional leaching with the same strength acid gave a negligible further yield of inorganic phosphorus, which indicated that a virtually complete extraction was obtained by the procedure outlined.

<div align="center">RESULTS</div>

<div align="center">*Dephosphorylation of calcium glycerophosphate*</div>

The rapid hydrolysis of calcium glycerophosphate by the exoenzyme of roots and the widespread use of glycerophosphates in fixation studies suggested the desirability of studying this organic phosphate in incubation tests with toluene-treated soil. The conditions that had been found optimal for the glycerophosphatase of corn roots (pH 4.0 and 45°C.) were employed, and two series of tests were made. As can be seen from the results in table 2, remarkably similar results were obtained from the two series, 66.2 to 66.9 per cent of the 210 p.p.m. of organic phosphorus which was added being mineralized in 18 hours.

<div align="center">*Effect of H-ion concentration and of temperature on dephosphorylation of yeast nucleic acid*</div>

The behavior of nucleic acid in contact with soil was studied in more detail. The effects of soil reaction and temperature on the rate of dephosphorylation of nucleic acid by soil catalysts are shown in figure 1.

The H-ion concentration of pH 6.9 and a temperature of 60°C. were optimum for the release of phosphorus from nucleic acid by soil catalysts in 14- to 18-hour tests at an initial concentration of 212 p.p.m. organic phosphorus. A much slower rate of decomposition of nucleic acid was obtained at 45°C. and optimum acidity than was observed with calcium glycerophosphate in this soil. At similar initial concentrations of organic phosphorus, a maximum mineralization of 20 per cent was obtained in 18 hours, compared with 66 per cent hydrolysis

of calcium glycerophosphate. The soil catalysts involved in the dephosphorylation of nucleic acid were more sensitive to changes in acidity than of tempera-

TABLE 2

Dephosphorylation of calcium glycerophosphate by soil catalysts

SAMPLE NUMBER	TREATMENT OF SAMPLE	CONCENTRATION OF INORGANIC PHOSPHORUS				MINERALIZATION OF ORGANIC P*
		Before incubation		After incubation		
		Ave. duplicate determinations	Minus control	Ave. duplicate determinations	Minus control	
		p.p.m. P	p.p.m. P	p.p.m. P	p.p.m. P	per cent
Series 1						
1	Soil + toluene + Ca-glycerophosphate solution†	21.0	0	168.0	139.0	66.2
2	Soil + toluene + H₂O	30.0	....	29.0	.....	
Series 2						
1	Same as No. 1 above	20.0	0	171.5	140.5	66.9
2	Same as No. 2 above	20.4	....	31.0	.....	

* Initial concentration of organic phosphorus, 210 p.p.m. P.

† Ca-glycerophosphate solution plus toluene showed a negligible concentration of inorganic phosphorus before and after incubation.
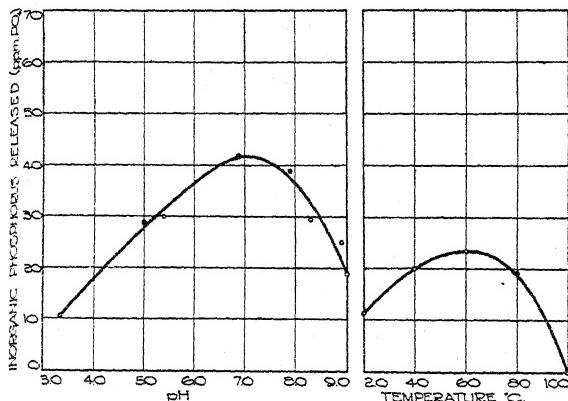
FIG. 1. EFFECTS OF pH AND TEMPERATURE ON DEPHOSPHORYLATION OF NUCLEIC ACID BY SOIL CATALYSTS

Initial concentration of organic phosphorus was 212 p.p.m. P. The pH curve was obtained from 18-hour incubations at 45°C.; temperature curve from 14-hour incubations at pH 7.0.

ture, and their activity fell off more rapidly on the alkaline side of neutrality than in the acid range. The shape of the activity curve in the acid range could be attributed in part to the fact that the optimum reaction for one of the enzymes

in the nuclease system is about pH 4.0. The fact that the activity curves obtained for the nuclease system showed more buffering over a wide range of conditions than did similar curves that were reported (14) for glycerophosphatase activity may be explained by the dependence of the rate of release of inorganic phosphorus on the velocities of two distinct reactions.

Two observations that were made on the effect of temperature on the controls that were run in these tests should be noted. The samples of toluene-treated soil plus distilled water showed about 28 p.p.m. of 10 per cent HCl-extractable inorganic phosphorus when incubated at temperatures between 20 and 80°C. but yielded 54 p.p.m. inorganic phosphorus when held at 100°C. for 18 hours. Thus an increase in incubation temperature from 80 to 100° nearly doubled the amount of acid-soluble inorganic phosphorus in this soil. The second observation was that nucleic acid solutions plus the antiseptic (without soil) showed slight chemical decomposition (1.5 per cent) at 90° and considerable breakdown (20 per cent) at 100°C. The freshly prepared solutions, however, were stable at the lower temperatures.

DISCUSSION

The optimum reaction for dephosphorylation of nucleic acid by both root-borne enzymes (14) and soil catalysts (as found in this investigation) was shown to be between pH 6.2 and 7.0. The high sensitivity of enzymatic reactions to slight amounts of inhibitors could easily account for the slight difference in optimum H-ion concentrations for the catalysts from the two sources. Likewise a maximum release of inorganic phosphorus from this compound was obtained at 60°C. by both soil- and root-borne catalysts. The strong similarity between the behavior of the soil system and that of the root-borne enzymes suggests that at least part of the catalytic power of soil originated in plant residues. The extent to which plant roots account for the catalyzing action of soil in effecting the hydrolysis of urea and organic phosphates cannot be determined from the information available at this time. There is the possibility that the extracellular enzymes of microorganisms may accumulate in soils, and even though the living microbial processes are halted by the antiseptic used in these tests, it is conceivable that some enzymatic activity could persist. A study of the effect of cropping treatment and the addition of materials to stimulate microbiological activity on the catalytic properties of soils should help to explain the nature and origin of these catalysts.

Several investigators have used salts of glycerophosphoric acid in studies (1, 5, 11, 15, 16)[4] on rates of decomposition and penetration of organic phosphates in soil, looking to a possible use of some of these compounds as commercial fertilizers. It was hoped to obtain a better distribution of phosphorus in the soil by their use, thus increasing the positional availability of the phosphate.

Conrad (1) allowed solutions of various organic phosphorus compounds to percolate through a column of pots of soil and cropped the soils to measure phos-

[4] Spencer, V. E. *Ibid.*

phorus retention. He found that Yolo subsoil retained phytin but not glycero-phosphates, whereas Aiken surface soil retained both of these compounds and also sodium nucleinate. As an explanation of the retention of the last compound, he suggested that it may have been converted to the relatively insoluble magnesium salt. The retention of glycerophosphates by the surface soil and not by the subsoil, as well as the retention of the phosphorus of nucleic acid, could be explained by assuming catalytic hydrolysis of these compounds and subsequent chemical fixation of the inorganic phosphate. Subsoils would not be expected to exhibit the catalytic powers of surface soils in which larger amounts of plant residues are present, if these catalysts are of an organic nature.

Hilbert, et al. (5) found such a rapid rate of fixation of glycerophosphate by Cecil clay that they concluded that the phosphate was held in some manner in the organic form by the soil colloids. The same workers reported that heating another soil (Las Vegas loam) destroyed its high rate of fixation of glycerophos-phate and advanced this as evidence that mineralization by microorganisms in some soils must precede fixation of this organic phosphate.

Kaolin has been reported (6) to be effective in adsorbing glycerophosphatase. Ensminger and Gieseking (4) found proteolytic hydrolysis of proteins to be reduced by bentonite adsorption, but kaolinite in a similar role had no effect on the decomposition of these same compounds.

Investigators do not agree as to the possibility of obtaining better penetration in soils with organic phosphates than with inorganic forms. Spencer and Stewart (16) claimed that better penetration was obtained with the organic forms, whereas Pinck, Sherman, and Allison (11) reported rapid colloidal adsorption of some of the same compounds. Köttgen (7) and Scharrer and Keller (15) failed to obtain any better distribution or availability of phosphorus with organic phosphates than with inorganic carriers.

The disagreement among investigators on the relative penetrating ability of some of the organic phosphates in different soils is more understandable in the light of the results of these studies on the catalytic properties of soils. Varying amounts of hydrolytic catalysts in the different soils may account in part for the inconsistency of reports on the behavior of any given organic compound.

If agricultural soils in general possess the vigorous mineralizing action on glycerophosphates which was exhibited by the sample of Ames fine sandy loam used in these studies, there is little reason to expect much better penetration of these organic compounds than of mineral phosphates under field conditions. It follows also that this would hold true for any of the organic phosphates which are subject to hydrolysis by the same catalysts as the glycerophosphates. They would be expected to undergo dephosphorylation rather rapidly in soils, quite independently of an active micropopulation.

Any attempt to explain the behavior of organic phosphorus compounds when added to untreated soil should take into account three major factors that will largely determine the distribution and rate of fixation of the compounds in the soil. These factors are (a) physical sorption of the compound in its original form by soil colloids, (b) catalytic decomposition independent of microbial

activity, and (c) availability of the compound to soil microorganisms. Evidently these agencies will assume varying degrees of importance in different soils. In soils where either physical adsorption or catalytic hydrolysis is highly operative for any particular compound, that source of phosphorus would not show much better penetration or distribution than the inorganic phosphates.

SUMMARY

Calcium glycerophosphate when incubated at pH 4.0 and 45°C. in toluene-treated soil underwent 66 per cent mineralization in 18 hours from an initial concentration of 210 p.p.m. of organic phosphorus.

Dephosphorylation of nucleic acid by soil catalysts was only about one third as rapid as the breakdown of calcium glycerophosphate when optimum conditions for the respective systems were maintained.

It was found that the optimal reaction (pH 6.2–7.0) and temperature (about 60°C.) for the dephosphorylation of nucleic acid by soil catalysts were about the same as the optimums that had been previously reported for the root-borne nuclease system.

The significance of the presence in soils of catalysts capable of dephosphorylating organic phosphate compounds is discussed with special reference to the possible value of organic phosphate fertilizers in obtaining better penetration of phosphates in soils.

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THE NATURE AND PROPERTIES OF PEATS IN NEW JERSEY[1]

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The nature and the type of peat produced in a given region are markedly affected by geographic, geologic, topographic, climatic, and other conditions. The resulting peat is controlled by the vegetation which gave rise to it, and the vegetation in its turn is influenced by the composition of the waters flowing into the bog and by the aforementioned conditions. In a recent survey of the peat resources of New Jersey (15, 16), cognizance was taken of these facts. This paper presents a summary of the findings of that survey.

The study of New Jersey peats dates to just a century ago, when the Legislature of the State established its first geological survey (10). Later and more detailed studies have been made by many of the noted state geologists; namely, Cook (2, 3, 4), Salisbury (11), McCourt (9), Vermeule (13, p. 75), Smock (12), and Lewis and Kümmel (8). Many of these studies have been limited to the utilization of peat for fuel or other purposes.

GEOGRAPHY AND GEOLOGY OF NEW JERSEY

The State of New Jersey forms a part of the North American Atlantic slope, lying within two geographic and geologic regions, the Coastal Plain and the Appalachian Province. The latter is usually subdivided into the Piedmont Plateau, the Appalachian Mountains or the New Jersey Highlands, and the Appalachian Valley. The Coastal Plain includes the southern part of the state, namely, the region south of a line running diagonally across the state through Trenton and New Brunswick. The Piedmont Plateau is bounded in New Jersey by the Hudson River in the east, by the Delaware River in the west, by the Coastal Plain in the south, and by the Highlands in the northwest. The Highlands are bounded on the northeast by New York State, on the south by the Piedmont Plateau, on the southwest by the Delaware River, and on the northwest by the irregular line of the Appalachian Valley which occupies the remainder of the state and which contains subordinate ridges, such as Kittatinny Mountain.

The Coastal Plain is a region of slight relief, the greatest elevation being 400 feet. The slope is generally to the southeast, the plain consisting chiefly of beds of clay, sand, gravel, and other rocks of Cretaceous, Tertiary, and Quaternary age. The Plateau is underlain by Triassic strata, with which are associated volcanic and intrusive igneous rocks; this is a region of gently rolling hills studded with trap ridges. First and Second Mountains constitute the

two most notable ridges in the plain, and the Palisades, along the Hudson River, form a third trap ridge. The region known as the Highlands resolves itself into four distinct parallel ranges: the Hudson, the Passaic, the Central Highland, and the Allamuchy-Pohatcong. These ranges are separated by the Wanaque, the German-Longwood, the Sparta-Musconetcong and the Pohatcong Valleys. There are many other peaks and valleys, of secondary importance. The Appalachian Mountains consist mostly of highly metamorphosed rocks of pre-Cambrian age, namely, gneisses and schists, with some marble or crystalline limestone, and intrusive igneous rocks. The lower parts of the Appalachian Valley are chiefly underlain by Kittatinny limestone; the ridges that traverse the valley are composed largely of Martinsburg shale and slate. Kittatinny Mountain is composed of red sandstone and conglomerate.

The Wisconsin glaciation, the most recent of a series of glacial formations, covered New Jersey with ice in the form of a highly irregular line running from Perth Amboy to Belvidere. North of this line, the state is covered discontinuously with drift, composed of boulders, gravel, sand, and clay, which was picked up by the ice in one locality and deposited elsewhere. The drift, along the line of the southernmost extension of the ice, is designated as the terminal moraine, this portion being ordinarily thicker than elsewhere. Peat formation has been affected by the terminal moraine, the ground moraine or till, the glacial streams and ice dams, and many other formations, such as kames, eskers, valley trains, moraine plains, and kettle formations.

TYPES OF PEAT IN NEW JERSEY

The whole state was found in this survey to contain 527,769 acres of peatland, representing about 8 per cent of the total surface area. Of the area mapped as peatland, 57 per cent (300,825 acres) proved to contain peat, whereas the remaining 43 per cent consists of mineral soil or has only a very shallow organic layer. The peats of the state were found to belong to four types. Of the total peat areas, 15.65 per cent (47,106 acres) were classified as sedge and reed peat, 23.45 per cent (70,585 acres) as forest peat, 13.26 per cent (39,912 acres) as fresh-water alluvial peats, and 47.64 per cent (143,222 acres) as tidal marsh peat. Although sphagnum plants are growing abundantly in the state, sphagnum peat is present in only very small quantities or is heavily admixed with reed and sedge or with forest peat material.

The dominant types of peat in New Jersey may be characterized as follows: *Sedge and reed peat*, often referred to as "humus," "muck," or "lowmoor peat," is usually dark brown to black when exposed to the air, and brown below the surface layer. Wood layers are commonly present in the profile. The reaction of this type of peat is between pH 4.5 and 6.8; the total nitrogen is 2.0 to 3.5 per cent on a dry basis, and the organic matter content varies between 70 and 95 per cent on a dry basis.

Forest peat, also known, in a marketable state, as forest litter, forest mold, oak leaf mold, tree mold, and peat mold, varies in formation depending on underlying or admixed strata. Its reaction ranges between pH 3.8 and 5.5, the total nitro-

gen between 1.0 and 2.5 per cent, and the ash content between 3 and 20 per cent on a dry basis.

Fresh-water alluvial peats are high in mineral matter, the organic matter content varying from 20 to 60 per cent, on a dry basis. The nitrogen also varies considerably, usually between 0.2 and 1.5 per cent.

Tidal marshes usually contain coarse fibrous material together with large amounts of inorganic sediment. Woody layers are commonly present. The reaction of these peats, as well as their chemical composition, is extremely variable.

Predominance of peat types in various regions of the state

The different peat types are not uniformly distributed through the different sections of the state, because of differences in the composition of the ground water, nature of substrate, and other factors.

The lowmoor type or sedge and reed peat is most common in the Kittatinny Valley, where it may or may not be underlain by deposits of calcareous marl. Save in very few instances, calcareous marl has not been found outside the Great Valley. In some cases there is considerable admixture of forest peat in the sedge and reed deposits. The tidal marsh peat is invariably found in regions of salt or brackish water. Many of the bogs found inland, in the Coastal Plain, contain alluvial deposits, but the great majority of true peats in the fresh-water bogs are of the forest type.

The mountain regions almost invariably give rise to forest peat bogs, usually containing reeds and sedges. Alluvial peats are common. The Piedmont Plateau contains sedge and reed peats with an abundance of forest material, and, in many cases, also alluvial matter.

Although in the survey, the state was divided into 21 peat-bearing regions based on the dominant rivers and brooks, only a few representative areas will be discussed here.

Northern, predominantly sedge and reed, peats. Among the various types of peat occurring in the bogs of New Jersey, the sedge and reed type has received the greatest consideration, since this peat has found extensive application for the growth of agricultural crops and as a source of humus for improving soils poor in organic matter. These New Jersey peats are similar, both in origin and in chemical composition, to the typical sedge and reed or lowmoor peats of Europe. The New Jersey bogs vary greatly in depth, from 2 to more than 35 feet. Many of the peat profiles are formed almost entirely by sedges and reeds, whereas others have an admixture of forest material. Some are underlain by clay, pebbles, or sedimentary material; others by calcareous marl or rock. Some have a deep aquatic layer, whereas in others this stratum is shallow or even absent. Some are overlain on the surface by an alluvial layer, which may vary in depth from a few inches to several feet; in others, the alluvial stratum may be absent or may occur within the profile. This is brought out in figure 1 and in tables 1 and 2.

Although the most typical sedge and reed peats occur in the northern part

of the state, some are also found in the central and southern sections. Many of these bogs can be drained and result in excellent truck-producing soils. The
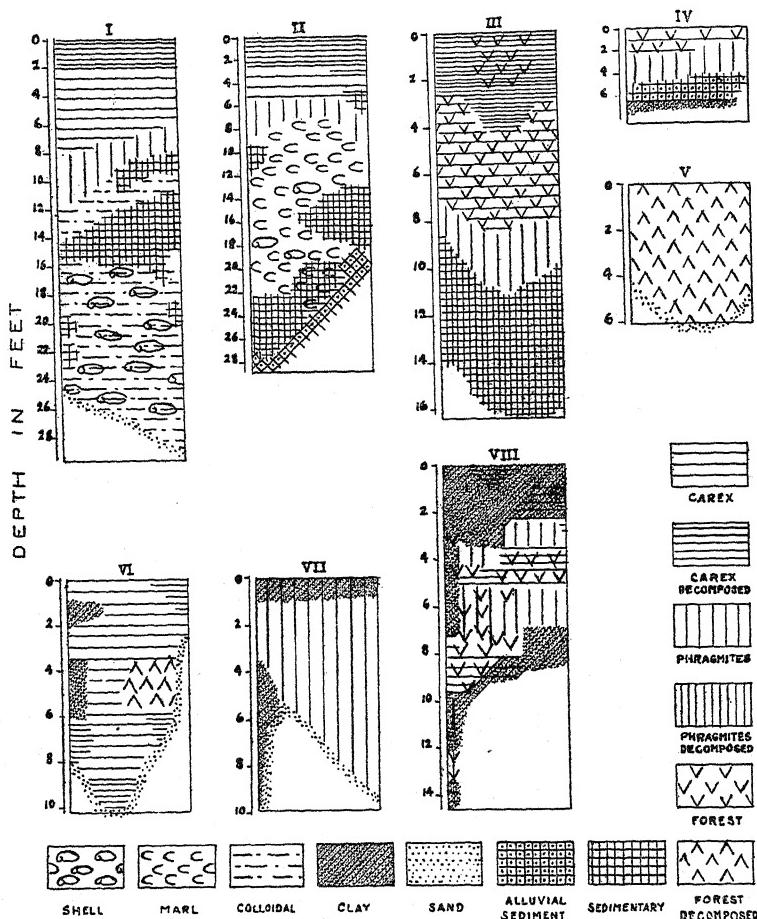
FIG. 1. SOME TYPICAL PROFILES OF NEW JERSEY PEATS

I. Profile of a typical north Jersey bog, with abundance of shells in the sedimentary layer.

II. North Jersey sedge and reed peat with a very deep marl layer.

III. North Jersey forest peat, with considerable sedge and reed material, without marl.

IV. Shallow bog in north Jersey mountain region representing mixed sedge and reed and forest peat.

V. Typical forest peat found in south Jersey.

VI. Profile of tidal marsh bog in south Jersey.

VII. Another tidal marsh, with increasing amount of clay and silt.

VIII. Tidal marsh representing mixture of sedge and reed and forest peat, with abundance of alluvial material.

acidity of these peats (pH 5.0 to pH 6.0) is ordinarily not great, and the addition of lime for crop growth is unnecessary in many instances. Some may even

be alkaline in reaction (pH 7.5 to 8.0), when calcareous marl underlies the organic strata.

TABLE 1

Profile of the source bog of Paulinskill River

DEPTH	DESCRIPTION OF MATERIAL	MOISTURE	ASH*	NITROGEN*	pH
feet		*per cent*	*per cent*	*per cent*	
0–1	Black, granulated, crumbly, well-decomposed material	86.0	8.0	3.29	5.1
0–6	Dark brown, coarse, fibrous and matted reed and sedge peat	88.9	7.8	2.61	5.5
6–7	Dark brown, coarse, fibrous and matted reed and sedge peat	89.8	6.5	2.73	6.3
7–9	Dark brown, coarse, fibrous and matted reed and sedge peat	90.6	6.4	2.57	6.7
9–10	Brown, fibrous and matted reed and sedge peat	91.9	12.2	3.37	6.8
11–12	Gray sedimentary peat, shells and calcareous marl	85.9	57.9	1.41	7.8
12–13	Gray sedimentary peat, shells and calcareous marl	80.9	76.1	1.04	8.0
16–17	Gray-brown liver peat with shells	83.6	62.6	1.43	8.0
18–19	Chocolate-brown liver peat	89.4	39.1	2.43	7.9
19–20	Gray-brown liver peat	85.3	58.9	1.48	7.8
20–21	Brown liver peat	89.2	42.7	2.31	7.8
21–22	Chocolate-brown liver peat with a few shells	90.0	30.8	2.78	7.9
24–25	Gray clay	44.6	94.8	0.18	8.0

* On dry basis.

TABLE 2

Profile of Cedar Swamp on Kittatinny Mountain

DEPTH	DESCRIPTION OF SAMPLE	MOISTURE	ASH*	NITROGEN*	pH
feet		*per cent*	*per cent*	*per cent*	
0–4	Brown, well-decomposed forest peat	81.0	5.7	1.65	4.2
4–7	Brown forest and reed and sedge peat	90.8	2.3		5.5
7–9	Brown forest peat	90.7	2.3		6.1
9–10	Brown reed and sedge peat	90.3	31.4		6.2
10–11	Green sedimentary peat and sand				
11–12	Gray sand				

* On dry basis.

The peat deposits with limestone bottoms found in the northernmost region of the state offer typical examples of sedge and reed peats underlain by calcareous marl. In those cases where the bogs are located in the higher portions of the valley, on slate and sandstone bottoms, the peat generally contains more wood, and the marl layer is scanty or absent.

An excellent example of the sedge and reed type underlain by calcareous marl is found in the important bog embracing approximately 1400 acres and extending from Newton to Branchville Junction. This deposit is on the limestone in the great depression that extends from the Delaware River to the Hudson River; sandstone and slate ridges form, for the most part, the sides of the long axis of the area, which extends from northeast to southwest. Limestone knolls and glacial deposits bound the bog to the southwest. At the northeastern extremity is found a part of the notable Balesville recessional moraine, which was formed when the ice was in retreat, and which has a maximum width of three-quarters of a mile. The moraine, laid down in the vicinity of Warbasse, dammed the waters of this part of the valley, giving rise to a fairly deep lake, which, with the passage of time, became converted into a peat bog.

The average depth of peat in this deposit is 14 feet; the greatest depth, 30 feet. The peat is typical of the sedge and reed lowmoors, although there is some admixture of forest material. The surface foot, except along the main brook (the Paulinskill, where alluvial deposits were found), consists of well-decomposed black material. The lower succeeding stratum consists mainly of brown sedge and reed peat, although sunken logs are frequently encountered, some layers being definitely of a forest type. Beneath this is an aquatic layer, consisting largely of liver peat, containing, as well as alternating with, shell strata. Considerable woody peat is found in some portions of the bog.

In the southern part of the bog, the pH rises from 5.8 in the surface foot to 6.5 in the 8- to 11-foot stratum; thereafter, the presence of lime, in the form of shells, results in a sudden rise in pH to 7.6, which then remains virtually constant. The nitrogen content of this peat varies, on a dry basis, from 2.46 per cent, in the 3- to 7-foot layer, to 3.14 per cent in the 17- to 19-foot layer. The ash content is high in the surface stratum, decreases from 31 to 3 per cent in the seventh foot, increases to 8 per cent in the 8- to 11-foot stratum, and rises to 81 per cent in the shell layer. The ash content of the light brown liver peat is 26 per cent; this increases to 67 per cent in the stratum of greenish brown liver peat. The high content of mineral matter in the surface layer is due to the admixture of alluvial material, which covers part of this southern section of the bog to considerable depths.

In the northern part of the bog, fibrous reed and sedge peat of excellent quality is found to a depth of 10 feet. The ash content decreases from 8 per cent at the surface to 6.5 per cent in the sixth foot, and increases again to 12.2 per cent in the ninth foot. The nitrogen content is 3.3 per cent at the surface, decreases with depth to an average of 2.6 per cent at the ninth foot, and again increases to 3.4 per cent. The pH values increase from 5.1 at the surface to 6.8 in the ninth foot. From the tenth foot downward, a sudden marked decrease in organic matter content occurs. The presence of calcareous marl, in greater or lesser amount, is responsible for the increase in pH value, the increase in ash content, and the decrease in nitrogen content with increasing depth.

In other parts of the bog are found alternating layers of shell gyttja and liver

peat, the strata of clay gyttja occurring near the clay substrate. Several profiles of this bog were used in earlier analyses of the organic matter composition of lowmoor peats (14).

The relationship between the geologic formation on which the peat deposit occurs and the types of peat produced in the deposit is clearly demonstrated in a bog extending south from Balesville. This bog is situated in the sandstone and shale hills rising above the Paulinskill bog previously described, and is only 1½ miles from the latter area. The difference in elevation between these two areas is slight. The former bog is 524 feet above tide, whereas the Balesville bog is 600 feet above sea level. Both bogs owe their origin to the damming effect of the Balesville recessional moraine; on the one hand, a limestone valley was flooded, and, on the other, water was backed up into a slate and sandstone valley.

The aquatic layers vary from green to brown and consist of either sedimentary or liver peats; no shells or calcareous deposits are present. The aquatic peat strata are overlain by reed sedge and woody peats, which, at the surface, have undergone considerable decomposition. The pH values vary between narrow limits, 5.5 and 6.0, thereby differing markedly from those of the Newton bog and indicating absence of an excess of lime. The pH value of the ground water of the Balesville bog is 6.8; that of the ground water of the Newton bog is 7.6 to 8.0. It would appear logical to assume that the higher pH value at the latter bog is due to greater lime content.

Forest peats of northern New Jersey. The forest peats of northern New Jersey are almost invariably found in the mountainous regions, where the absence of limestone or of lime-rich glacial drift and the operation of climatic and other factors have resulted in the growth of white-cedar, swamp-pine, rhododendron, hemlock, and other forest plants that have given rise to typical forest peats. An example of these peats is found in a forest bog called "Cedar Swamp," on Kittatinny Mountain. This mountain, although geographically a high ridge of the Appalachian Valley, contains peat deposits of the forest type that differ in no respect from those of the Highlands of New Jersey.

Cedar Swamp, situated less than a mile northeast of Lake Marcia and within a few hundred yards of the New Jersey-New York boundary line, is the northernmost bog in New Jersey. Its elevation, some 1500 feet above sea level, is exceeded by no bog in New Jersey. The drainage region that supplies Cedar Swamp with a limited quantity of surface or subsurface water is extremely small; it appears probable that the bog is, in the main, fed by spring water from the Catskill Mountains, as is Lake Marcia. The bog drains down the mountain into New York State, the water eventually finding its way into the Wallkill River.

The bog vegetation is typical of northern cedar bogs; cedars and rhododendron largely replace the deciduous shrubs and trees of the valley bogs. Glacial till and stratified drift are found on this part of Kittatinny Mountain, which is approximately 1½ miles wide between the steep eastern and western slopes. The bog lies in a ravine at the head of a steep slope to the north. It appears

certain that glacial till blocked the ravine, resulting in the formation of a 30-acre lake.   The presence of a certain amount of stratified drift is indicated by the sand found beneath a part of the bog.

This bog contains a typical forest peat, characterized by a low ash content below the surface stratum, a low nitrogen content of 1.65 per cent, and a fairly acid reaction, the pH values varying from 4.2 to 6.2.   The forest peats of northern New Jersey do not normally attain the low pH values of similar bogs in the southern part of the state, but, in the main, the ash values are lower.

Forest peats of southern New Jersey.   The forest peats of southern New Jersey occur, almost without exception, in the region of the pine barrens, which form a large part of the Coastal Plain.   Many of the differences between the bogs of the barrens and those of the remainder of the plain may be attributed to the preservation of the pine barrens, together with the typical Coastal Plain vegetation, as an island, whereas the remainder of the Coastal Plain was submerged beneath the sea.

TABLE 3

Profile of central part of Great Cedar Swamp, Dennis Creek drainage region

DEPTH	DESCRIPTION OF SAMPLE	MOISTURE	ASH*	pH
feet		*per cent*	*per cent*	
0–1†	Forest peat	79.3	6.3	3.6
1–3	Forest peat	83.5	3.7	3.6
3–6	Forest peat	81.4	2.4	3.6
6–8	Forest peat and sand	85.7	19.2	3.9
8–9	Sand, clay, and woody material			
9–10	Sand bottom			

* On dry basis.
† Nitrogen content of surface foot is 1.79 per cent, on dry basis.

The forest peats in this region are covered both by coniferous and by deciduous vegetation, but during the peat-forming period virtually all of the bogs must have been covered by white cedars.   In many of the bogs deciduous trees are now dominant, but this is due to the cutting of the cedar trees during recent times.   According to Harshberger (5), the white cedars of the cedar swamp make such dense growth as to be tolerated by only the most shade-loving plants. Three noteworthy facts regarding these impressive forests were indicated; namely, the protective effect of the impenetrable growth against wind, the cooling effect produced by the dense shade and the water-saturated sphagnum moss during the hot months, and the relative warmth of the forests during the cold periods of the year.

Great Cedar Swamp, in which head Dennis and Cedar Swamp Creeks, is typical of the present New Jersey pine-barren bogs (table 3).   Where lumbering has occurred, deciduous trees are dominant, although scattered white cedars are present everywhere; where the footing was so insecure as to prohibit wood cutting, as in the vicinity of the huge tidal marshes, the white cedar dominates

the flora, and the growth represents the true white-cedar forest. This bog constitutes one of the largest and one of the potentially most important cedar swamps in southern New Jersey. Some 6 miles long and 1 to 2 miles wide, it extends to the tidal marshes of both Delaware Bay and Tuckahoe River. Approximately half of the bog is drained to the southwest by the headwaters of Dennis Creek, the remainder draining to the northeast by way of Cedar Swamp Creek. This bog appears to constitute a remnant of the huge white-cedar forests which may have fringed the state and which are now, for the most part, buried under many feet of tidal marsh peat and sand. Great Cedar Swamp lies at the extreme southern boundary of the pine barrens. Since the regional soils in and out of the pine barrens are similar, and since the topography of the two regions in this limited area of the state does not differ, the peat found in this bog is identical with the forest peats found in the heart of the pine barrens.

Great Cedar Swamp, in common with many of the coastal cedar forests, has changed to a remarkable extent during the past century. Leavitt (7), wrote in 1867:

> Cedar Swamp creek, which runs in Tuckahoe river, and Dennis creek, which runs into Delaware bay, head in the same swamp; and the whole length of the two streams—a distance of seventeen miles—is one continuous cedar swamp. The wood is the white cedar. It grows on peat, and its roots run near the surface. In the present growth of standing timber, scarcely any trees are to be found more than one hundred years old; but these rest upon a formation containing we know not how many generations of trees which have lived and fallen before them. Large stumps are found frequently standing directly on other large logs, and with their roots growing all around them, and then other logs still under these; so that one soon becomes perplexed in trying to count back to the time when the lower ones were growing.

At the present time, this bog has shrunk to little more than one third of its former length, the greater portion having been covered by tidal marshes. These marshes must be underlain by considerable depths of forest peat; because of lack of time, however, they were not surveyed. Great Cedar Swamp contains forest peat of low ash content, to a maximum depth of 10 feet. The stratum adjacent to the sand bottom consists of an admixture of aquatic peat, clay, and sand. Despite the extent of the bog, the analytical results obtained from a single profile are representative.

Tidal marsh and alluvial peats. Among the peat formations of New Jersey, the tidal marshes occupy a unique place, because of the rather extensive and tortuous coast line. The rivers bring down to the sea large quantities of sediments. On coming in contact with the salty water, the latter, especially the colloidal particles, are precipitated. In these areas a characteristic association of plants develops (6), which in turn is converted into a peat material with a high ash content. This type of peat formation is favored by the raised beaches, which the sea continuously builds up, as well as by the slow subsidence of the shore line, a process further accentuated by the action of the tides. These supply a large part of the inorganic materials, whereas the characteristic vegetation contributes to the organic constituents of the peat.

The tidal marshes in New Jersey have long attracted attention, but it was not until the end of the last century that attempts were made to throw light upon the origin and nature of these formations. Cook (1), who made the first careful survey of the peat areas of the state, observed a definite correlation between the formation of marshes and land subsidence. He cited many instances of buried stumps and tree trunks found at all depths above the subsoil during ditch-digging operations. Where the marsh had recently been cut away by water action, numbers of stumps were left exposed.

The relationship between tidal marsh and submerged cedar forests is excellently illustrated in the Maurice River marshes. From head of tide at Millville, to Delaware Bay, woody peat is everywhere present, overlain by greater or lesser depths of tidal marsh peat. All of this land-locked marsh was reclaimed in the

TABLE 4

Profile of tidal marsh peat, Maurice River drainage region

DEPTH	DESCRIPTION OF SAMPLE	MOISTURE	ASH*	pH
feet		*per cent*	*per cent*	
0-1†	Reed, sedge, woody, and alluvial peat	83.5	45.8	5.4
1-2	Reed, sedge, and woody peat	84.8	16.6	4.8
2-4	Reed, sedge, and woody peat	87.0	27.0	4.8
4-5	Reed, sedge, woody and alluvial peat	78.9	61.7	5.2
5-7	Reed, sedge, woody, and alluvial peat	84.9	57.7	4.9
7-11	Tidal marsh peat and clay			
11-13	Clay			
13-15	Macerated forest peat and clay	86.8	24.5	3.4
15-16	Macerated forest peat and clay	71.6	68.0	3.4
16-17	Sand bottom			

* On dry basis.
† Nitrogen content of surface sample is 1.82 per cent, on dry basis.

past; some of this land has been lost probably through compacting and flooding. In that part of the river west of Port Elizabeth, 7 feet of tidal clays and peats cover 5 feet of woody and alluvial peat (table 4). In the same region, slightly above high tide, a small bog contains fresh-water peat overlying tidal peat, which, in turn, covers peat of fresh-water origin. The original fresh-water peat became covered by tidal deposits; local changes elevated the tract above the level of high tide, and forest peat was again able to form.

Cedar logs, in a state of excellent preservation, are found in the vicinity of Port Norris. Such logs have recently been mined in an area midway between Port Norris and Mauricetown, on the west bank of the Maurice River. From the disposition of the white-cedar logs, it appears certain that five distinct cedar forests are superimposed upon one another. The tidal marsh reaches depths of more than 40 feet; it tends to shoal out near the edge of Delaware Bay, where, it would appear, shoals or barrier beaches were formed at some time in the past. The analyses of another tidal marsh are given in table 5.

The group of marshes along the lower reaches of the Delaware River, as well as similar marshes elsewhere, form transition groups between the fresh-water alluvial bogs and the tidal marshes. Peats belonging to this type have been found in all sections of the state.   In the northern regions, this type of peat formation is usually found along the banks of streams where periodic flooding has deposited alluvial material.   The peat is characterized by a high mineral content; the inorganic constituents are mixed with the organic material in colloidal state or in the form of residues of sedges, wood, or other plant debris.   In some instances colloidal, sedimentary and forest strata are present, but in every case the mineral content is high.

TABLE 5

Profile of Swanby tidal marsh, Mullica River drainage region

DEPTH	DESCRIPTION OF SAMPLE	MOISTURE	ASH*	pH
feet		*per cent*	*per cent*	
0–1	Reed and sedge peat containing clay	67.0	72.9	3.5
1–2	Reed and sedge peat containing clay	77.4	54.5	2.1
2–3	Reed and sedge peat containing clay	86.9	29.0	3.5
3–4	Reed and sedge peat containing clay and wood	88.2	13.9	4.5
4–5	Reed and sedge peat containing clay and wood	90.5	30.4	3.1
5–8	Reed and sedge peat containing clay and wood	90.0	21.8	5.5
8–9	Reed and sedge peat, clay, and sand	75.5	65.9	5.1
9–10	Sand bottom	26.1	97.0	4.8

* On dry basis.

Characteristic properties of various peat types in New Jersey

In order to summarize the characteristics of the different peat formations in the state, a large number of representative areas were selected.   The data for depth, ash content, nitrogen content, and pH values were averaged.   In addition to the four major divisions outlined above, these peat types were subdivided on the basis of (*a*) the presence of submerged forest peat in tidal areas, (*b*) combinations of two or more of the main peat types, (*c*) the presence of the dominant type in the two different geographic regions of the state, and (*d*) the presence or absence of calcareous marl in the peat profile.

In averaging the various data, many samples taken throughout the region under consideration were used.   Of the tidal peats, for example, 58 areas comprising 41,418 acres in all parts of the tidal regions of the state were selected. In these 58 tidal areas, the following numbers of analyses were available for preparing the average: 226 for ash, 228 for pH values, and 43 for nitrogen.   Since the peat bogs of the northern part of New Jersey are of much lesser magnitude than those of the southern part, the aggregate acreage involved is less, although the number of analyses available for mathematical treatment is large.   Thus, of the northern reed and sedge peats, 77 areas totaled only 5,217 acres; 454 analyses of ash values were available for the fibrous strata and 175 for the sedimentary

strata. For these two strata, 652 pH determinations were made and 101 nitrogen analyses. In the case of certain nitrogen values, insufficient determinations were available for proper averages.

TABLE 6

Depth, organic matter and nitrogen contents, and pH values of a series of typical peat bogs in New Jersey

NAME OF BOG	AREA	DEPTH	ORGANIC MATTER, DRY BASIS		NITROGEN DRY BASIS	pH		
			Surface foot	Greater depth	Surface foot	Surface foot	Greater depth	
	acres	feet	per cent	feet	per cent			feet	
Swartswood Lake (area 2)	25	7	60.9	3–4	82.6	1.92	5.3	3–4	5.3
Swartswood Lake (area 3)	60	22	56.9	10–11	28.7	2.46	4.6	10–11	6.4
Wallpack Bog	5	22	85.9	9–10	90.4	2.97	5.4	9–10	5.7
Kittatinny Lake	10	10	63.4	4–5	67.3	2.45	4.3	4–5	5.1
Branchville (Culvers Lake)	78	19	72.4	9–10	43.1	2.74	5.6	9–10	6.6
Budd Lake (area 1a)	347	10	65.9	4–5	94.5	2.63	5.5	4–5	5.0
Budd Lake (area 1b)	347	34	85.7	16–17	30.7	1.05	4.9	16–17	5.7
Glovers Pond	5	9	87.5	3–4	75.5	3.01	6.7	3–4	6.5
Greendell Bog	238	22	86.3	10–11	94.6	3.70*	6.3	10–11	6.7
Laurel Pond	23	18	64.9	9–10	75.5	1.78†	5.5	9–10	6.4
Beariens Bog	6	17	83.4	7–8	91.8	3.11	5.6	7–8	5.8
Culvers Lake Swamp	73	4	29.0	2–3	93.9	0.83	6.3	2–3	5.6
Pine Swamp	102	17	94.6	8–9	96.2	2.03	5.0	8–9	5.1
Pine Swamp	37	18	94.5	8–9	94.4	1.83	4.2	8–9	5.0
Burnt Fly Swamp	235	7	73.8	2–3	37.3	1.14	4.5	2–3	4.1
Lakewood area 1	520	6	87.8	2–3	91.8	1.64‡	4.5	2–3	4.3
Lake Carasaljo (Lakewood area 3)	9	6	87.9	2–3	92.4	1.70	4.5	2–3	5.0
Hope Bog	17	25	82.0	12–13	52.6	3.09	6.3	12–13	8.3
Andover Bog	21	8	83.5	3–4	90.5	2.78	6.5	3–4	6.2
Troy Meadows	100	7	64.5	4–5	71.7			4–5	6.0
Columbia Meadows	538	5	47.2	2–3	69.2	1.67	5.3	2–3	5.5
Black Meadow	740	11	76.1	5–6	47.5	2.71	5.6	5–6	6.0
Bridgeton	475	5	29.7	2–3	17.8		4.8	2–3	4.8
Springdale	8	15	78.5	7–8	89.0	3.39	6.4	7–8	7.6
Silver Lake	1	21	70.0	8–9	20.4	2.58	6.2	8–9	8.2

* 2–3 feet.

† 4–6 feet.

‡ 1–2 feet.

It is impossible to consider peat of any given bog as being pure in type. A bog containing predominantly reed and sedge peat ordinarily contains also woody material, or even forest strata; the presence of this material will, therefore, be shown in the various analyses. In this mathematical survey, bogs in all parts of the state were carefully selected for dominant type, but all extraneous and subordinate strata were included in the proper averages; thus, an alluvial reed and

sedge stratum, occurring in a forest bog, was averaged with the forest stratum, in order to indicate the actual condition of the bog.

In many instances, throughout the state, the layer forming the present surface of the bog contains large amounts of alluvial material, although peat of excellent quality may occur beneath the more recent strata. In other cases, alluvial strata are found sandwiched between fibrous or woody peats. In a single bog, great variation may also be found in the pH and in the nitrogen values. A core obtained from a buried tree trunk, for example, may, in a bog predominantly reed and sedge in nature, result in analytical values indicative of the forest peats. Since the greatest deviation occurs between the nonaquatic and the aquatic strata, the separation of these strata brought about a correction of the largest source of error in computation.

Table 6 gives certain pertinent data for a number of individual bogs distributed throughout the state. More detailed information on the location of these bogs, the drainage conditions, and the vegetation will be found in the complete report (16).

UTILIZATION OF NEW JERSEY PEATS

The peat lands of New Jersey have been utilized for many different purposes, among which are the following: pasture or hay; field and truck crops; cranberries or blueberries; reservoirs, lakes, parks, game reserves, etc.; mining of bog iron ore; mining of cedar logs; timbering; gathering of sphagnum moss; removal of sedge and reed peat for upland soil improvement; removal of "orchid peat" and of leaf mold.

The region draining into the lower Delaware River and Delaware Bay is notable for the extent of land that was once utilized for hay production or for pasture and later abandoned. Almost 50 per cent of all the land in the entire state known to have been utilized for this purpose is found in this region, which marked the earliest and most extensive attempts at marshland reclamation. Much of the reclaimed land has since been lost to the tides. The region contains 14 per cent of all areas at present devoted in part to hay and pasture in the state, and, together with the drainage regions of the Navesink and Maurice Rivers and of Cohansey Creek, embraces 31 per cent of the state totals; an additional 50 per cent of all areas are found in the regions drained by the Wallkill, Raritan, Pequest, Paulinskill, and Passaic Rivers. The remaining 19 per cent are evenly distributed in other parts of the state. In the northern part of the state comparatively slight amounts of hay are cut from peat areas, the land being utilized primarily for pasture. In southern New Jersey, on the other hand, particularly on the reclaimed tidal marsh, large quantities of hay are cut each year.

The same considerations which applied to the hay crop cause the lower Delaware region to lead in land abandoned after cropping, and in the same proportion. At the present time, 16 per cent of those areas devoted in part or whole to field and truck cropping is in the Delaware, Maurice, Navesink, and Rancocas regions; in the north an additional 50 per cent is in the Passaic, Paulinskill, Pequest, Raritan, and Wallkill regions.

Five regions: namely, Barnegat, Metedeconk, Mullica, Rancocas, and Tucka-hoe, contain 91 per cent of the areas that were devoted to cranberry culture and later abandoned. At this time, 93 per cent of the active bogs are found in the Barnegat, Mullica, Rancocas, and Tuckahoe regions.

In southern New Jersey, reservoirs for the flooding of cranberry bogs are common. In some cases the reservoirs may become permanent lakes, or old bogs may be permanently flooded for recreational purposes. In northern New Jersey, artificial lake formation is essentially for recreational purposes, other uses being subordinate. Some peat and alluvial lands have been flooded to provide water for dairy herds; other boglands form part of large metropolitan water reservoirs.

Industries have made use of the marshland in the vicinity of our large tide-water cities; thus, 69 per cent of all areas utilized in part or whole for industrial or residential purposes lie in the drainage depressions of the lower Delaware, Hackensack, Passaic, and Raritan Rivers.

Information is too incomplete to permit charting the extent of the former bog iron industry in New Jersey. It is known that the Mullica and Great Egg Rivers contained the bulk of iron ore.

The mining of cedar logs took place on a fairly extensive scale along the Maurice River and Dennis Creek. It is probable that cedar was mined in other places, but here again, information is incomplete. Lumbering on the bogland, on the other hand, has been, and still is so extensive that no attempt has been made to evaluate the industry, which is, for the most part, conducted by individual owners. It is probable that no bog of any extent in the entire state has escaped lumbering operations. White cedar is the most valuable product of the pine-barren bogs; much white cedar was formerly removed from the forest bogs of the mountainous regions of northern New Jersey, together with hemlock and other trees.

Large quantities of sphagnum moss are gathered from the pine-barren forest bogs; as is the case with lumbering, the work is, for the most part, that of numerous natives of the region, and every bog has probably been stripped of its sphagnum cover at some time in the past. In northern New Jersey, although sphagnum moss occurs, little is gathered and the main surface crop consists of the roots of the cinnamon fern, often called "orchid peat." In the pine-barren region a lesser crop is the leaf mold which forms to depths as great as 18 inches over some of the low uplands, and which provides excellent mulching material for certain acid-loving plants.

SUMMARY

This paper presents a survey of the peat resources of the State of New Jersey. The peatlands of the state cover about 8 per cent of the total surface area. The bogs vary greatly in depth, origin, and chemical composition of the peat.

The peat types of the state are divided into four groups: sedge and reed peat, forest peat, fresh-water alluvial peat, and tidal marsh. Moss peat is entirely absent, although sphagnum is growing on the surface of many peat areas in the state.

The sedge and reed, or lowmoor peats, predominate in the northern or glaciate areas of the state, whereas the forest peats and the salt marshes predominate in the southern or Coastal Plain areas.

The peats have been extensively utilized for various agricultural and industrial purposes depending upon the nature of the peat and upon the drainage conditions and geographical location of the bogs.

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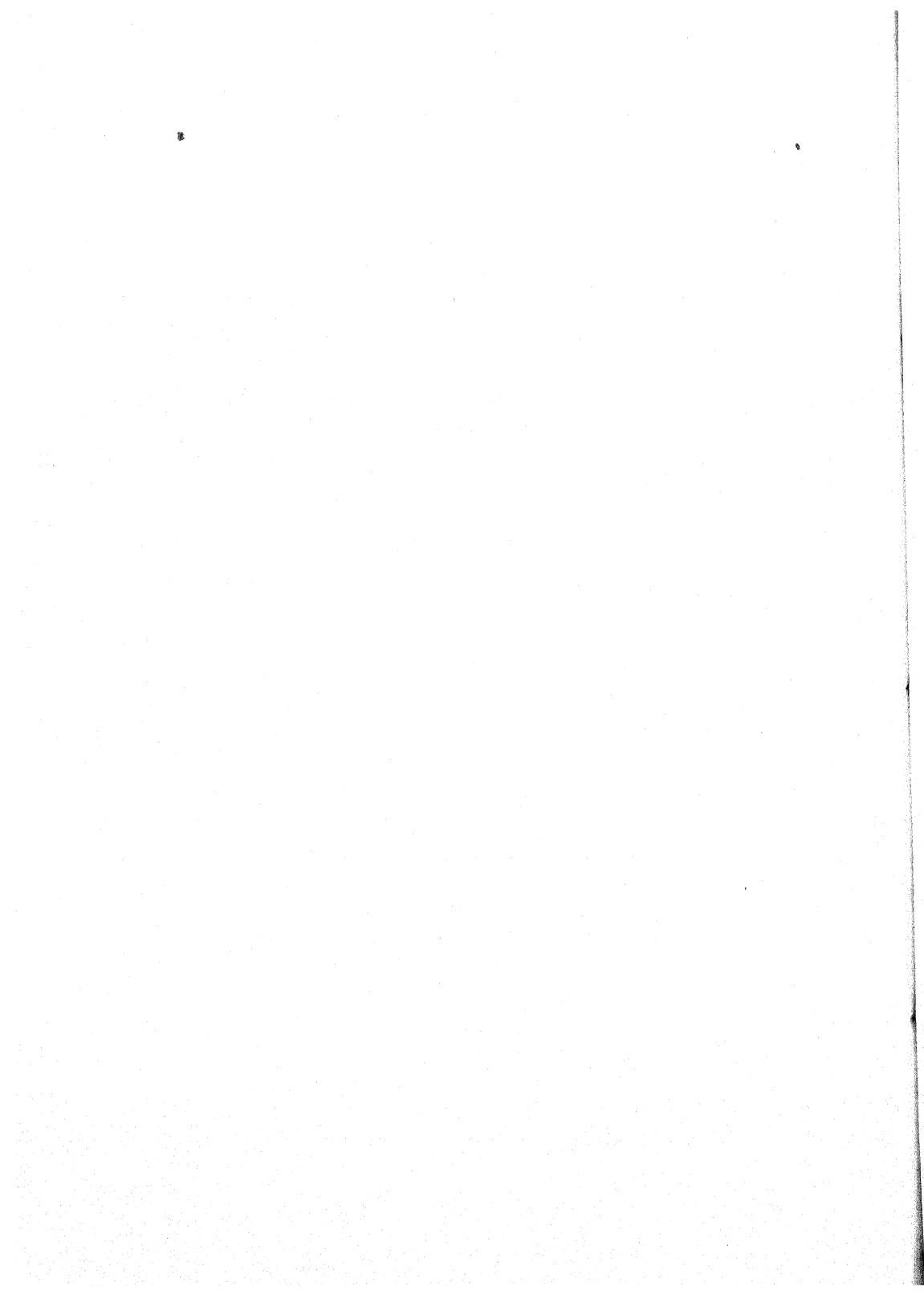
ZINC RELATIONSHIPS OF SOME UTAH SOILS

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Recent surveys of Utah show symptoms of zinc deficiency to be widespread. Sweet cherries, apricots, peaches, apples, and plums have been found with little-leaf, or rosette, similar to the disease reported in other parts of the United States (1, 3, 5, 10). The afflicted trees have responded to injections and sprays containing zinc salts. No data have been published concerning the zinc contents of soils or plants in Utah.

Most of the valley soils of north central Utah have been derived from limestone materials and are calcareous in at least a part of the profile. But many small areas of noncalcareous soils occur which are usually near parent bodies of such rocks as granite, gneiss, or quartzite. Trees showing evidence of zinc deficiency in this part of the state have always been found growing on soils formed predominantly from such rocks. In only two cases have zinc deficiencies been noted in trees growing on calcareous soils, and in these instances the soils are derived largely from granitic materials with some mixing of limestone.

The present study was initiated to determine why zinc-deficiency symptoms are so closely associated with noncalcareous soils in this area.

SOIL SAMPLES

The soils studied are in orchards and fields in north central Utah that have been cultivated for some time. Samples were taken from the sides of freshly dug pits. One sample was taken from the topsoil at each location. This varied in depth from 12 to 18 inches. A second sample was obtained from the upper subsurface, which included the 12-inch depth below the topsoil. A third sample was taken at each location from the lower subsurface, which extended 12 to 18 inches below the upper subsurface horizon. In addition, some samples were taken from a few subhorizons having special features.

In two instances little-leaf was found limited to trees in definite zones of orchards. In these two cases two sets of profile samples were obtained from zinc-deficient areas and two from the zinc-sufficient areas. In the other orchards studied, little-leaf occurrence was so general that no paired samples could be obtained. In the noncalcareous soils, 11 soil profiles were sampled in the zinc-deficient areas and 4 soil profiles in zinc-sufficient areas. As most of the noncalcareous soils sampled have not been surveyed, series names are unavailable.

The calcareous soils investigated were selected as representative of soils derived from limestone materials. One profile each was sampled from Woodrow clay loam, Taylorsville silty clay loam, Salt Lake sandy loam, Orem loam, and Millville loam soil. Samples of granite, gneiss, quartzite, and limestone formations representative of the parent rocks of the soils studied were also included

in the investigation.[1]   Care was taken to prevent contamination of samples by metals that might contain zinc.

EXPERIMENTAL METHODS

Samples were prepared for total zinc determination by fusion with potassium pyrosulfate according to the procedure outlined by Hibbard (6).   Hibbard's procedure was also employed for the determination of available zinc by extracting 5-gm. samples of soil with two successive 400-ml. portions of 0.05 N KCl acidified with acetic acid to pH 3.2.   Zinc was determined in aliquots of the solutions by the modification of the dithizone method suggested by Caughey, Holland, and Ritchie (2) except that color comparisons were made with an Aminco Type F electrophotometer.   In some cases the results obtained by color comparisons were checked by titration with a standard bromine solution.   Precautions suggested by Hibbard (8) and by Caughey, Holland, and Ritchie (2) were followed to remove zinc from reagents and equipment.

Organic matter was determined by the modification of the H_2CrO_4-oxidation method proposed by Purvis and Higson (11).   The pH values were determined in a soil-water paste (about 2:1) with a Beckman pH meter.

RESULTS

The average total and available zinc contents of the various groups of soils investigated are shown in table 1.   Seventy-two soil samples were included in the study.   The data indicate that calcareous soils of this area contain almost twice as much total zinc and considerably more available zinc than do the noncalcareous soils.   There is also an indication that a greater proportion of the total zinc in the profile accumulates in the topsoil of noncalcareous soils than of calcareous soils.

The quantities of total and available zinc in soils from areas of orchards showing symptoms of little-leaf are not significantly lower than the quantities in soils where deficiency symptoms are not evident.   In the two orchards where samples were obtained from both zinc-deficient and zinc-sufficient areas, however, significantly more zinc was found where little-leaf symptoms were not evident.

Table 2 gives the analysis of rock samples representative of rock formations in this area.   It is evident that there is no distinct difference in the total zinc content of the limestone and siliceous rocks studied.   The initial zinc content of the soil parent material could not account, then, for the present zinc status of the soils investigated.   Since no measurable amount of zinc could be extracted from the limestone samples by the KCl-HAc solution, whereas small amounts were extracted from the granite, gneiss, and quartzite, there is probably a difference in removal of zinc from these two classes of rocks during the weathering process.   A rapid removal of zinc from gneiss by weathering is indicated by the analysis of a partly weathered rock from the Kaysville area, as shown at the

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[1] Members of the geology department of Utah State Agricultural College cooperated in obtaining these samples.

bottom of table 2. This difference in zinc removal during weathering was investigated to a limited extent, but lack of any adequate criterion of time or degree of weathering of rock samples made the results difficult to interpret.

TABLE 1

Average zinc content of various groups of Utah soils

(Parts per million)

SOIL DEPTH	NONCALCAREOUS SOILS				CALCAREOUS SOILS	
	Zinc-deficient areas		Zinc-sufficient areas			
	Total	Available	Total	Available	Total	Available
Topsoil......................	146	5.9	181	6.03	301	12.4
Upper subsurface..............	117	2.6	101	3.40	265	10.4
Lower subsurface..............	81	2.6	87	4.03	238	10.5

TABLE 2

Zinc content of various rocks

TYPE OF ROCK	SOURCE	CaCO₃ CONTENT	TOTAL ZINC	AVAILABLE ZINC
		per cent	*p.p.m.*	*p.p.m.*
White marl (Pliestocene—Bonneville)	White Valley, Utah	56.6	578	0.0
Limestone (Miss.—Brazer)	Big Cottonwood Canyon	42.0	673	0.0
Limestone (Miss.—Brazer)	Big Cottonwood Canyon	42.8	518	0.0
Fresh water algal limestone (Eocene—Flagstaff)	Thistle Canyon	37.9	550	0.0
Limestone (Pliocene?—Salt Lake)	Collinston area	31.0	652	0.0
Limestone (Miss.—Madison)	Providence Canyon	38.2	528	0.0
Gneiss (Archaeozoic—Farmington Canyon complex)	Kaysville area	....	725	1.0
Quartzite (Algonkian)	Cottonwood Canyon	....	345	1.2
Quartzite (Penna.—Oquirrh)	Provo Canyon	....	527	0.0
Quartzite (Cambrian—Brigham)	Bakers Canyon, Brigham	....	871	4.0
Granite (Cottonwood—Tertiary)	Alpine	....	750	8.4
Gneiss, partly weathered (Archaeozoic—Farmington Canyon complex)	Kaysville area	....	285	8.5

The average organic matter content and pH values of the various groups of soil are given in table 3. The data for each soil sample were used to calculate the simple correlation coefficients given in table 4. The data for the two calcareous, zinc-deficient soils were not used in these calculations because these soils were composed largely of granitic materials with only slight mixing of limestone. The correlation coefficients for all samples, as given at the bottom

of table 4, indicate highly significant relationships between total zinc and organic matter, between total zinc and pH, and between total zinc and available zinc, and a significant correlation between available zinc and pH.   An examination of the correlation coefficients between each of these pairs of analytical results for the individual groups of soil samples reveals, however, that the correlation values for all samples may be misleading.   This is illustrated by the correlation coefficients between total zinc and organic matter.   Organic matter is highest

TABLE 3

Average organic matter content and pH values of various groups of Utah soils

	NONCALCAREOUS SOILS				CALCAREOUS SOILS	
SOIL DEPTH	Zinc-deficient areas		Zinc-sufficient areas			
	Organic matter	pH	Organic matter	pH	Organic matter	pH
	per cent		*per cent*		*per cent*	
Topsoil.....................	1.97	7.18	2.51	7.00	2.10	8.18
Upper subsurface.............	0.90	7.32	0.50	7.32	1.21	8.21
Lower subsurface.............	0.42	7.53	0.38	7.39	0.71	8.31

TABLE 4

Correlation coefficients between various soil values within groups of Utah soil samples

SOIL SAMPLES	NUMBER OF SAMPLES	TOTAL ZINC AND ORGANIC MATTER	AVAILABLE ZINC AND ORGANIC MATTER	TOTAL ZINC AND pH	AVAILABLE ZINC AND pH	TOTAL ZINC AND AVAILABE ZINC
Topsoil, noncalcareous soils......	15	0.207	0.399	0.339	0.060	−0.155
Topsoil, calcareous soils..........	5	0.801	0.746	0.824*	−0.565	0.498
Topsoil, all soils.................	20	0.197	0.393	0.543*	0.296	0.392
Subsurface, noncalcareous soils...	34	0.339*	−0.02	−0.191	−0.311	−0.035
Subsurface, calcareous soils......	15	0.195	−0.032	0.103	−0.336	−0.053
Subsurface, all soils..............	49	0.341*	0.183	0.470**	0.349**	0.565**
All samples†.....................	69	0.485**	0.112	0.428**	0.275*	0.520**

* Significant to the 5 per cent point.

** Significant to the 1 per cent point.

† The highly significant correlations with "all samples" are misleading and result largely from distinct differences between groups of samples. (See discussion.)

in the surface soils, and in most samples zinc tends to be higher in the surface. When topsoils alone are considered, however, there is no significant relationship between the two characteristics. Significant correlations are observed for the noncalcareous subsurface soils and all subsurface soil samples. The individual data indicate that these correlations largely result from relatively high zinc and organic matter contents of five of the upper subsurface samples. Similarly, the highly significant correlations between total and available zinc in all subsurface samples and in all soil samples seem to be the result of the higher total and

available zinc in the calcareous soils than in the noncalcareous soils, and to the generally larger quantities in the topsoils in comparison with the subsurface soils. For the remainder of the groups of soil samples the correlations between total and available zinc were not significant, and in three cases the trend was slightly toward a negative relationship.

DISCUSSION

Any comparison of the data presented here with those obtained in other investigations must take into consideration the method of soil sampling. Thus, Hibbard (7, 8) found a close relationship between organic matter and zinc accumulation in soil. The soil samples used in Hibbard's study, however, were obtained largely from soils which had never been cultivated, whereas the samples employed in the present study were from cultivated orchards and fields. The organic matter contents of the samples used in this study, then, are probably more closely related to recent soil management practices than to virgin conditions.

Zinc extracted from the soils by the KCl-HAc solvent of pH 3.2 had little if any advantage over determination of total zinc in indicating zinc deficiency in the soils studied. The study was not designed, however, to test the value of this method of analysis. If the study had been confined to paired samples of zinc-deficient and zinc-sufficient soils within the same orchards, a better test would have been made of the method. So far as the data obtained are concerned, field study of soil texture and parent material may be as reliable an indication of probable zinc deficiency as any of the analyses made.

In general, the results indicate that zinc deficiency is not likely to be widespread on calcareous soils in Utah. This condition is different from that observed by Alben and Boggs (1) in Texas and Louisiana. They found there that the zinc content of basic soils is usually higher than that of acid soils, but that trees rosette more on basic soils. Lott (9) also reported an increase in available zinc with a decrease in the pH of the soil. In the present study, however, the lowest pH encountered was 6.2 and the highest 9.1. The slight degree of acidity encountered was probably insufficient to affect appreciably zinc availability. Chandler (4) found that trees growing on soils high in clay and with reactions as high as pH 8 to 9 rarely showed zinc deficiency, whereas trees on sandy, well-drained soils with reactions as low as pH 5.9 showed deficiency symptoms.

It is difficult to separate the effect of soil texture from that of parent material in the results of the present study. Soils derived from granite, gneiss, and quartzite are generally sandy. And soils derived largely from limestone usually contain appreciable quantities of clay. The only sandy, calcareous soil studied was Salt Lake sandy loam. This soil contained about 240 p.p.m. of zinc, which was below the average for calcareous soils but was 20 to over 100 per cent above that for the noncalcareous soils studied. The noncalcareous soils investigated were sandy loams or gravelly loams.

SUMMARY

In Utah, zinc-deficiency symptoms usually appear on fruit trees growing on noncalcareous soils derived principally from granite, gneiss, quartzite, or related rocks. No zinc-deficiency symptoms have been observed on soils derived principally from limestone.

The zinc content of calcareous soils was found to be almost twice that of noncalcareous soils. Samples of rock which serve as parent materials for noncalcareous soils contained about the same amount of zinc as samples of various formations of limestone. The zinc in the granite, gneiss, and quartzite samples studied was more soluble than that in limestone. Apparently, zinc is lost more rapidly from silicate rocks than from limestone rocks during weathering processes.

In the soils studied, no consistent correlations were found between values for any of the four factors determined: total zinc, available zinc, organic matter, and pH.

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